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METHODS FOR CHEMICAL ANALYSIS OF WATER AND WASTES

ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
Environmental Research Center
Cincinnati, Ohio 45268

U.S. ENVIRONMENTAL PROTECTION AGENCY
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FOREWORD

The accomplishment of our objectives in protecting the environment requires an awareness of the interdependence of the components we seek to protect—air, water, and land. Through individual and joint efforts the National Environmental Research Centers provide this multidisciplinary focus through programs engaged in

> studies on the effects of environmental contaminants on man and the biosphere,
>
> the development of efficient means of monitoring these contaminants, and
>
> a search for more effective ways to prevent undesirable modification of the environment and the recycling of valuable resources.

This chemical methods manual was developed by the staff of the Environmental Monitoring and Support Laboratory, formerly known as the Methods Development and Quality Assurance Research Laboratory (MDQARL) of the National Environmental Research Center, Cincinnati, to provide methodology for monitoring the quality of our Nation's waters and to determine the impact of waste discharges. The test procedures have been carefully selected to meet the needs of laboratories engaged in protecting the aquatic environment. The contributions and counsel of scientists in other EPA laboratories are gratefully acknowledged.

The manual is published and distributed by the Office of Technology Transfer, as one of a series designed to insure that the latest technologies developed by EPA and private industry are disseminated to states, municipalities and industries who are responsible for environmental pollution control.

The other manuals in this series are:

> *Handbook for Monitoring Industrial Wastewater*
>
> *Handbook for Analytical Quality Control in Water and Wastewater Laboratories.*

These are also available through the Office of Technology Transfer, Cincinnati, Ohio 45268.

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INTRODUCTION

This second edition of "Methods for Chemical Analysis of Water and Wastes" contains the chemical analytical procedures used in U.S. Environmental Protection Agency (EPA) laboratories for the examination of ground and surface waters, domestic and industrial waste effluents, and treatment process samples. Except where noted under "Scope and Application," the methods are applicable to both water and wastewaters, and both fresh and saline water samples. The manual provides test procedures for the measurement of physical, inorganic, and selected organic constituents and parameters. Methods for pesticides, industrial organic waste materials, and sludges are given in other publications of the Agency. The methods were chosen through the combined efforts of the EPA Regional Analytical Quality Control Coordinators, the staff of the Physical and Chemical Methods Branch, Methods Development and Quality Assurance Research Laboratory, and other senior chemists in both federal and state laboratories. Method selection was based on the following criteria:

(1) The method should measure the desired property or constituent with precision, accuracy, and specificity sufficient to meet the data needs of EPA, in the presence of the interfering materials encountered in water and waste samples.

(2) The procedure should utilize the equipment and skills available in modern water pollution control laboratories.

(3) The selected method is in use in many laboratories or has been sufficiently tested to establish its validity.

(4) The method should be rapid enough to permit routine use for the examination of a large number of samples.

Instrumental methods have been selected in preference to manual procedures because of the improved speed, accuracy, and precision. In keeping with this policy, procedures for the Technicon AutoAnalyzer have been included for laboratories having this equipment available.

Precision and accuracy statements are provided where such data are available. These statements are derived from interlaboratory studies conducted by the Quality Assurance and Laboratory Evaluation Branch, Methods Development and Quality Assurance Research Laboratory; the American Society for Testing Materials; or the Analytical Reference Service of the US Public Health Service, DHEW.

These methods may be used for measuring both total and dissolved constituents of the sample. *When the dissolved concentration is to be determined, the sample is filtered through a 0.45-micron membrane filter and the filtrate analyzed by the procedure specified.* The sample should be filtered as soon as possible after it is collected, preferably in the field. Where field filtration is not practical, the sample should be filtered as soon as it is received in the laboratory.

Many water and waste samples are unstable. In situations where the interval between sample collection and analysis is long enough to produce changes in either the concentration or the physical state of the constituent to be measured, the preservation practices in Table II are recommended.

This manual is a basic reference for monitoring water and wastes in compliance with the requirements of the Federal Water Pollution Control Act Amendments of 1972. Although other test procedures may be used, as provided in the Federal Register issue of October 16, 1973 (38FR 28758), the methods described in this manual will be used by the Environmental Protection Agency in determining compliance with applicable water and effluent standards established by the Agency.

Although a sincere effort has been made to select methods that are applicable to the widest range of sample types, significant interferences may be encountered in certain isolated samples. In these situations, the analyst will be providing a valuable service to EPA by defining the nature of the interference with the method and bringing this information to the attention of the Director, Methods Development and Quality Assurance Research Laboratory, through the appropriate Regional AQC Coordinator.

SAMPLE PRESERVATION

Complete and unequivocal preservation of samples, either domestic sewage, industrial wastes, or natural waters, is a practical impossibility. Regardless of the nature of the sample, complete stability for every constituent can never be achieved. At best, preservation techniques can only retard the chemical and biological changes that inevitably continue after the sample is removed from the parent source. The changes that take place in a sample are either chemical or biological. In the former case, certain changes occur in the chemical structure of the constituents that are a function of physical conditions. Metal cations may precipitate as hydroxides or form complexes with other constituents; cations or anions may change valence states under certain reducing or oxidizing conditions; other constituents may dissolve or volatilize with the passage of time. Metal cations may also adsorb onto surfaces (glass, plastic, quartz, etc.), such as, iron and lead. Biological changes taking place in a sample may change the valence of an element or a radical to a different valence. Soluble constituents may be converted to organically bound materials in cell structures, or cell lysis may result in release of cellular material into solution. The well known nitrogen and phosphorus cycles are examples of biological influence on sample composition.

Methods of preservation are relatively limited and are intended generally to (1) retard biological action, (2) retard hydrolysis of chemical compounds and complexes and (3) reduce volatility of constituents.

Preservation methods are generally limited to pH control, chemical addition, refrigeration, and freezing. Table 1 shows the various preservatives that may be used to retard changes in samples.

TABLE 1

Preservative	Action	Applicable to:
$HgCl_2$	Bacterial Inhibitor	Nitrogen forms, Phosphorus forms
Acid (HNO_3)	Metals solvent, prevents precipitation	Metals
Acid (H_2SO_4)	Bacterial Inhibitor	Organic samples (COD, oil & grease organic carbon), Nitrogen-phosphorus forms
	Salt formation with organic bases	Ammonia, amines
Alkali (NaOH)	Salt formation with volatile compounds	Cyanides, organic acids
Refrigeration	Bacterial Inhibitor, Retards chemical reaction rates	Acidity-alkalinity, organic materials, BOD, color, odor, organic P, organic N, carbon, etc., biological organism (coliform, etc.)

In summary, refrigeration at temperatures near freezing or below is the best preservation technique available, but it is not applicable to all types of samples.

The recommended choice of preservatives for various constituents is given in Table 2. These choices are based on the accompanying references and on information supplied by various Regional Analytical Quality Control Coordinators.

TABLE 2

RECOMMENDATION FOR SAMPLING AND PRESERVATION OF SAMPLES ACCORDING TO MEASUREMENT (1)

Measurement	Vol. Req. (ml)	Container	Preservative	Holding Time(6)
Acidity	100	P, G(2)	Cool, 4°C	24 Hrs.
Alkalinity	100	P, G	Cool, 4°C	24 Hrs.
Arsenic	100	P, G	HNO_3 to pH <2	6 Mos.
BOD	1000	P, G	Cool, 4°C	6 Hrs.(3)
Bromide	100	P, G	Cool, 4°C	24 Hrs.
COD	50	P, G	H_2SO_4 to pH <2	7 Days
Chloride	50	P, G	None Req.	7 Days
Chlorine Req.	50	P, G	Det. on site	No Holding
Color	50	P, G	Cool, 4°C	24 Hrs.
Cyanides	500	P, G	Cool, 4°C NaOH to pH 12	24 Hrs.
Dissolved Oxygen				
Probe	300	G only	Det. on site	No Holding
Winkler	300	G only	Fix on site	4-8 Hours

TABLE 2 (Continued)

Measurement	Vol. Req. (ml)	Container	Preservative	Holding Time(6)
Fluoride	300	P, G	Cool, 4°C	7 Days
Hardness	100	P, G	Cool, 4°C HNO_3 to pH <2	7 Days
Iodide	100	P, G	Cool, 4°C	24 Hrs.
MBAS	250	P, G	Cool, 4°C	24 Hrs.
Metals				
Dissolved	200	P, G	Filter on site HNO_3 to pH <2	6 Mos.
Suspended			Filter on site	6 Mos.
Total	100		HNO_3 to pH <2	6 Mos.
Mercury				
Dissolved	100	P, G	Filter HNO_3 to pH <2	38 Days (Glass) 13 Days (Hard Plastic)
Total	100	P, G	HNO_3 to pH <2	38 Days (Glass) 13 Days (Hard Plastic)

TABLE 2 (Continued)

Measurement	Vol. Req. (ml)	Container	Preservative	Holding Time(6)
Nitrogen				
Ammonia	400	P, G	Cool, 4°C H_2SO_4 to pH <2	24 Hrs.(4)
Kjeldahl, total	500	P, G	Cool, 4°C H_2SO_4 to pH <2	7 Days
Nitrate	100	P, G	Cool, 4°C H_2SO_4 to pH <2	24 Hrs.(4)
Nitrite	50	P, G	Cool, 4°C	24 Hrs. (4)
NTA	50	P, G	Cool, 4°C	24 Hrs.
Oil & Grease	1000	G only	Cool, 4°C H_2SO_4 or HCl to pH <2	24 Hrs.
Organic Carbon	25	P, G	Cool, 4°C H_2SO_4 to pH <2	24 Hrs.
pH	25	P, G	Cool, 4°C Det. on site	6 Hrs.(3)
Phenolics	500	G only	Cool, 4°C H_3PO_4 to pH <4 1.0 g $CuSO_4$/1	24 Hrs.
Phosphorus				
Ortho-phosphate, Dissolved	50	P, G	Filter on site Cool, 4°C	24 Hrs.(4)

TABLE 2 (Continued)

Measurement	Vol. Req. (ml)	Container	Preservative	Holding Time(6)
Hydrolyzable	50	P, G	Cool, 4°C H_2SO_4 to pH <2	24 Hrs.(4)
Total	50	P, G	Cool, 4°C	7 Days
Total, Dissolved	50	P, G	Filter on site Cool, 4°C	24 Hrs.(4)
Residue				
Filterable	100	P, G	Cool, 4°C	7 Days
Non-Filterable	100	P, G	Cool, 4°C	7 Days
Total	100	P, G	Cool, 4°C	7Days
Volatile	100	P, G	Cool, 4°C	7 Days
Settleable Matter	1000	P, G	None Req.	24 Hrs.
Selenium	50	P, G	HNO_3 to pH <2	6 Mos.
Silica	50	P only	Cool, 4°C	7 Days
Specific Conductance	100	P, G	Cool, 4°C	24 Hrs. (5)
Sulfate	50	P, G	Cool, 4°C	7 Days

TABLE 2 (Continued)

Measurement	Vol. Req. (ml)	Container	Preservative	Holding Time(6)
Sulfide	500	P, G	2 ml zinc acetate	24 Hrs.
Sulfite	50	P, G	Det. on site	No Holding
Temperature	1000	P, G	Det. on site	No Holding
Threshold Odor	200	G only	Cool, 4°C	24 Hrs.
Turbidity	100	P, G	Cool, 4°C	7 Days

1. More specific instructions for preservation and sampling are found with each procedure as detailed in this manual. A general discussion on sampling water and industrial wastewater may be found in ASTM, Part 23, p. 72-91 (1973).

2. Plastic or Glass

3. If samples cannot be returned to the laboratory in less than 6 hours and holding time exceeds this limit, the final reported data should indicate the actual holding time.

4. Mercuric chloride may be used as an alternate preservative at a concentration of 40 mg/1, especially if a longer holding time is required. However, the use of mercuric chloride is discouraged whenever possible.

5. If the sample is stabilized by cooling, it should be warmed to 25°C for reading, or temperature correction made and results reported at 25°C.

6. It has been shown that samples properly preserved may be held for extended periods beyond the recommended holding time.

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ACIDITY

STORET NO. 70508

1. Scope and Application
   1.1 This method is applicable to surface waters, sewages and industrial wastes, particularly mine drainage and receiving streams, and other waters containing ferrous iron or other polyvalent cations in a reduced state.
   1.2 The method covers the range from approximately 10 mg/1 acidity to approximately 1000 mg/1 as $CaCO_3$, using a 50 ml sample.
2. Summary of Method
   2.1 The pH of the sample is determined and a measured amount of standard acid is added, as needed, to lower the pH to 4 or less. Hydrogen peroxide is added, the solution boiled for several minutes, cooled, and titrated electrometrically with standard alkali to pH 8.2.
3. Definitions
   3.1 This method measures the mineral acidity of a sample plus the acidity resulting from oxidation and hydrolysis of polyvalent cations, including salts of iron and aluminum.
4. Interferences
   4.1 Suspended matter present in the sample, or precipitates formed during the titration may cause a sluggish electrode response. This may be offset by allowing a 15-20 second pause between additions of titrant or by slow dropwise addition of titrant as the endpoint pH is approached.
5. Apparatus
   5.1 pH meter, suitable for electrometric titrations.
6. Reagents
   6.1 Hydrogen peroxide (H_2O_2, 30% solution).
   6.2 Standard sodium hydroxide, 0.02 N.
   6.3 Standard sulfuric acid, 0.02 N.
7. Procedure
   7.1 Pipet 50 ml of the sample into a 250 ml beaker.
   7.2 Measure the pH of the sample. If the pH is above 4.0 add standard sulfuric acid in 5.0 ml increments to lower the pH to 4.0 or less. If the initial pH of the sample is less than 4.0, the incremental addition of sulfuric acid is not required.
   7.3 Add 5 drops of hydrogen peroxide.

7.4 Heat the sample to boiling and continue boiling for 2 to 4 minutes. In some instances, the concentration of ferrous iron in a sample is such that an additional amount of hydrogen peroxide and a slightly longer boiling time may be required.

7.5 Cool the sample to room temperature and titrate electrometrically with standard alkali to pH 8.2.

8. Calculations

8.1 Acidity, as mg/l $CaCO_3$ = $\frac{[(A \times B) - (C \times D)] \times 50{,}000}{\text{ml sample}}$

where:

A = vol. of standard alkali used in titration
B = normality of standard alkali
C = volume of standard acid used to reduce pH to 4 or less
D = normality of standard acid

8.2 If it is desired to report acidity in millequivalents per liter, the reported values as $CaCO_3$ are divided by 50, as follows:

$$\text{Acidity as meq/l} = \frac{\text{mg/l } CaCO_3}{50}$$

9. Precision

9.1 On a round robin conducted by ASTM on 4 acid mine waters, including concentrations up to 2000 mg/1, the precision was found to be ± 10 mg/l.

10. References

10.1 The procedure to be used for this determination can be found in:

ASTM Standards, Part 23, Water; Atmospheric Analysis, p 124, D-1067, Method E (1973).

Standard Methods for the Examination of Water and Wastewater, 13th Edition, p 370, Method 201 (Acidity and Alkalinity) (1971).

ALKALINITY (pH 4.5)

STORET NO. 00410

1. Scope and Application

   1.1 This method is applicable to drinking, surface, and saline waters, domestic and industrial wastes.

   1.2 The method is suitable for all concentration ranges of alkalinity; however, appropriate aliquots should be used to avoid a titration volume greater than 50 ml.

   1.3 Automated titrimetric analysis is equivalent.

2. Summary of Method

   2.1 An unaltered sample is titrated to an electrometrically determined end point of pH 4.5. The sample must not be filtered, diluted, concentrated, or altered in any way.

3. Comments

   3.1 The sample must be analyzed as soon as practical; preferably, within a few hours. Do not open sample bottle before analyses.

   3.2 Substances, such as salts of weak organic and inorganic acids present in large amounts, may cause interference in the electrometric pH measurements.

   3.3 Oil and grease, by coating the pH electrode, may also interfere, causing sluggish response.

4. Precision and Accuracy

   4.1 Forty analysts in seventeen laboratories analyzed synthetic water samples containing increments of bicarbonate, with the following results:

Increment as Alkalinity mg/liter, $CaCO_3$	Precision as Standard Deviation mg/liter, $CaCO_3$	Accuracy as Bias, %	Accuracy as Bias, mg/l, $CaCO_3$
8	1.27	+10.61	+0.85
9	1.14	+22.29	+2.0
113	5.28	- 8.19	- 9.3
119	5.36	- 7.42	- 8.8

(FWPCA Method Study 1, Mineral and Physical Analyses)

4.2 In a single laboratory (MDQARL), using surface water samples at an average concentration of 122 mg $CaCO_3$/1, the standard deviation was ±3.

5. References

5.1 The procedure to be used for this determination is found in:

Standard Methods for the Examination of Water and Wastewater, 13th Edition, p 52, Method 102, (1971).

ASTM Standards, Part 23, Water; Atmospheric Analysis, p 119, D-1067, Method B, (1973).

5.2 For samples having high concentrations of mineral acids, such as mine wastes and associated receiving waters, titrate to an electrometric endpoint of pH 3.9, using the procedure in:

ASTM Standards, Part 23, Water; Atmospheric Analysis, p 123, D-1067, Method D, (1973).

ALKALINITY

(Automated, Methyl Orange)

STORET NO. 00410

1. Scope and Application

    1.1 This automated method is applicable to drinking, surface, and saline waters, domestic and industrial wastes. The applicable range is 10 to 200 mg/l as $CaCO_3$.

    1.2 This method is not applicable to samples with pH lower than 3.1.

2. Summary of Method

    2.1 Methyl orange is used as the indicator in this method because its pH range is in the same range as the equivalence point for total alkalinity, and it has a distinct color change that can be easily measured. The methyl orange is dissolved in a weak buffer at a pH of 3.1, just below the equivalence point, so that any addition of alkalinity causes a loss of color directly proportional to the amount of alkalinity.

3. Sample Handling and Preservation

    3.1 Sample should be refrigerated at 4°C and run as soon as practical.

4. Interferences

    4.1 Sample turbidity and color may interfere with this method. Turbidity must be removed by filtration prior to analysis. Sample color that absorbs in the photometric range used will also interfere.

5. Apparatus

    5.1 Technicon AutoAnalyzer consisting of:

        5.1.1 Sampler I.

        5.1.2 Manifold.

        5.1.3 Proportioning pump.

        5.1.4 Colorimeter equipped with 15 mm tubular flow cell and 550 nm filters.

        5.1.5 Recorder equipped with range expander.

6. Reagents

    6.1 Methyl Orange: Dissolve 0.125 g of methyl orange in 1 liter of distilled water.

    6.2 pH 3.1 Buffer: Dissolve 5.1047 g of potassium acid phthalate in distilled water and add 87.6 ml 0.1 N HCl and dilute to 1 liter. Stable for one week.

    6.3 Methyl Orange-Buffered Indicator: Add 1 liter of pH 3.1 buffer to 200 ml methyl orange solution and mix well. Stable for 24 hours.

6.4 Stock Solution: Dissolve 1.060 g of anhydrous sodium carbonate (oven-dried at 140°C for 1 hour) in distilled water and dilute to 1000 ml. 1.0 ml = 1.00 mg $CaCO_3$.

6.4.1 Prepare a series of standards by diluting suitable volumes of stock solution to 100.0 ml with distilled water. The following dilutions are suggested:

ml of Stock Solution	Conc., mg/l as $CaCO_3$
1.0	10
2.0	20
4.0	40
6.0	60
8.0	80
10.0	100
18.0	180
20.0	200

7. Procedure

7.1 No advance sample preparation is required. Set up manifold as shown in Figure 1.

7.2 Allow both colorimeter and recorder to warm up for 30 minutes. Run a baseline with all reagents, feeding distilled water through the sample line. Adjust dark current and operative opening on colorimeter to obtain stable baseline.

7.3 Place distilled water wash tubes in alternate openings on sampler and set sample timing at 2.0 minutes.

7.4 Place working standards in sampler in order of decreasing concentration. Complete filling of sampler tray with unknown samples.

7.5 Switch sample line from distilled water to sampler and begin analysis.

8. Calculation

8.1 Prepare standard curve by plotting peak heights of processed standards against known concentrations. Compute concentration of samples by comparing sample peak heights with standard curve.

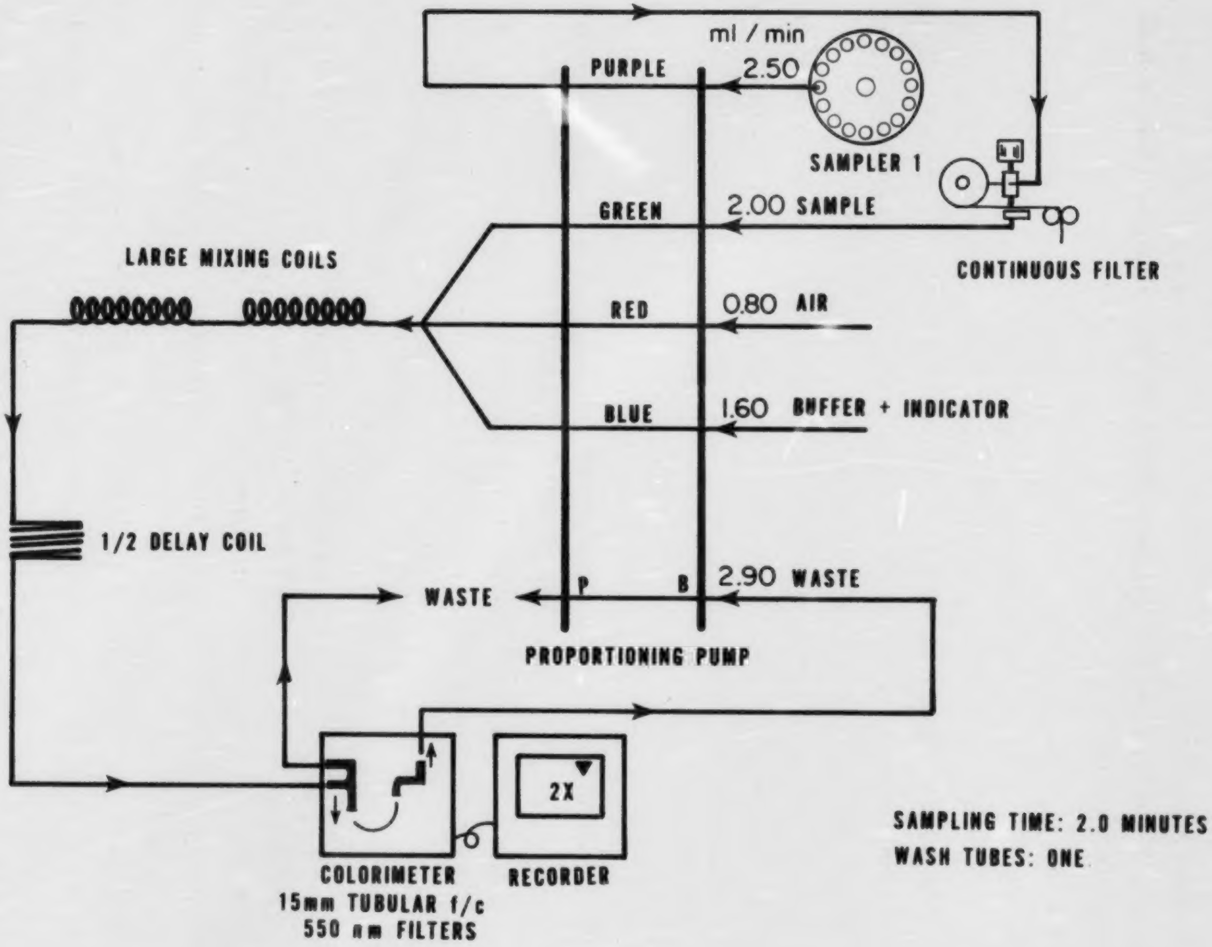
9. Precision and Accuracy

9.1 In a single laboratory (MDQARL), using surface water samples at concentrations of 15, 57, 154, and 193 mg/1 as $CaCO_3$ the standard deviation was ±0.5.

9.2 In a single laboratory (MDQARL), using surface water samples at concentrations of 31 and 149 mg/1 as $CaCO_3$ recoveries were 100% and 99%, respectively.

Bibliography

1. Technicon AutoAnalyzer Methodology, Bulletin 1261, Technicon Controls, Inc., Chauncey, N.Y. (1961).
2. Standard Methods for the Examination of Water and Wastewater, 13th Edition, p 52, Method 102 (1971).


ml / min
PURPLE
2.50
SAMPLER 1
GREEN
2.00 SAMPLE
CONTINUOUS FILTER
LARGE MIXING COILS
RED
0.80 AIR
BLUE
1.60 BUFFER + INDICATOR
1/2 DELAY COIL
WASTE
P
B
2.90 WASTE
PROPORTIONING PUMP
2X
COLORIMETER
15mm TUBULAR f/c
550 nm FILTERS
RECORDER

SAMPLING TIME: 2.0 MINUTES
WASH TUBES: ONE

FIGURE 1. ALKALINITY MANIFOLD AA-I

ARSENIC

STORET NO. Total 01002
Inorganic, Dissolved 00995
Inorganic, Total 00997

1. Scope and Application

1.1 The silver diethyldithiocarbamate method determines inorganic arsenic when present in concentrations at or above 10 μg/l. The method is applicable to most fresh and saline waters in the absence of high concentrations of chromium, cobalt, copper, mercury, molybdenum, nickel, and silver. Domestic and industrial wastes may also be analyzed after digestion (See 3.3).

1.2 Difficulties may be encountered with certain industrial waste materials containing volatile substances. High sulfur content of wastes may exceed removal capacity of the lead acetate scrubber.

2. Summary of Method

2.1 Arsenic in the sample is reduced to arsine, AsH_3, in acid solution in a hydrogen generator. The arsine is passed through a scrubber to remove sulfide and is absorbed in a solution of silver diethyldithiocarbamate dissolved in pyridine. The red complex thus formed is measured in a spectrophotometer at 535 nm.

3. Comments

3.1 In analyzing most surface and ground waters, interferences are rarely encountered. Industrial waste samples should be spiked with a known amount of arsenic to establish adequate recovery.

3.2 It is essential that the system be airtight during evolution of the arsine, to avoid losses.

3.3 If concentration of the sample and/or oxidation of any organic matter is required, refer to Standard Methods, 13th Edition, Method 104B, p 65, Procedure 4.a (1971).

3.3.1 Since nitric acid gives a negative interference in this colorimetric test, use sulfuric acid as a preservative if only inorganic arsenic is being measured.

3.4 l-Ephedrine in chloroform has been found to be a suitable solvent for silver diethyldithiocarbamate if the analyst finds the odor of pyridine objectionable [Anal. Chem. *45*, 1786 (1973)].

4. Precision and Accuracy

4.1 A synthetic unknown sample containing 40 μg/1, as As, with other metals was analyzed in 46 laboratories. Relative standard deviation was ±13.8% and relative error was 0%.

5. Reference

5.1 The procedure to be used for this determination is found in:

Standard Methods for the Examination of Water and Wastewater, 13th Edition, p 62, Method 104A (1971).

BIOCHEMICAL OXYGEN DEMAND
(5 Days, 20°C)

STORET NO. 00310

1. Scope and Application
   1.1 The biochemical oxygen demand test (BOD) is used for determining the relative oxygen requirements of municipal and industrial wastewaters. Application of the test to organic waste discharges allows calculation of the effect of the discharges on the oxygen resources of the receiving water. Data from BOD tests are used for the development of engineering criteria for the design of wastewater treatment plants.
   1.2 The BOD test is an empirical bioassay-type procedure which measures the dissolved oxygen consumed by microbial life while assimilating and oxidizing the organic matter present. The standard test conditions include dark incubation at 20°C for a specified time period (often 5 days). The actual environmental conditions of temperature, biological population, water movement, sunlight, and oxygen concentration cannot be accurately reproduced in the laboratory. Results obtained must take into account the above factors when relating BOD results to stream oxygen demands.
2. Summary of Method
   2.1 The sample of waste, or an appropriate dilution, is incubated for 5 days at 20°C in the dark. The reduction in dissolved oxygen concentration during the incubation period yields a measure of the biochemical oxygen demand.
3. Comments
   3.1 Determination of dissolved oxygen in the BOD test may be made by use of either the Modified Winkler with Full-Bottle Technique or the Probe Method in this manual.
   3.2 Additional information relating to oxygen demanding characteristics of wastewaters can be gained by applying the Total Organic Carbon and Chemical Oxygen Demand tests (also found in this manual).
4. Precision and Accuracy
   4.1 Eighty-six analysts in fifty-eight laboratories analyzed natural water samples plus an exact increment of biodegradable organic compounds. At a mean value of 2.1 and 175 mg/l BOD, the standard deviation was ±0.7 and ±26 mg/l, respectively. (EPA Method Research Study 3).
   4.2 There is no acceptable procedure for determining the accuracy of the BOD test.

5. References

5.1 The procedure to be used for this determination is found in:
Standard Methods for the Examination of Water and Wastewater, 13th Edition, p 489, Method 219 (1971).

BORON

(Curcumin Method)

STORET NO. 01022

1. Scope and Application
    1.1 This colorimetric method finds maximum utility for waters whose boron content is below 1 mg/1.
    1.2 The optimum range of the method on undiluted or unconcentrated samples is 0.1-1.0 mg/1 of boron.
2. Summary of Method
    2.1 When a sample of water containing boron is acidified and evaporated in the presence of curcumin, a red-colored product called rosocyanine is formed. The rosocyanine is taken up in a suitable solvent, and the red color is compared with standards either visually or photometrically.
3. Comments
    3.1 Nitrate nitrogen concentrations above 20 mg/1 interfere.
    3.2 Significantly high results are possible when the total of calcium and magnesium hardness exceeds 100 mg/1 as $CaCO_3$. Passing the sample through a cation exchange resin eliminates this problem.
    3.3 Close control of such variables as volumes and concentrations of reagents, as well as time and temperature of drying, must be exercised for maximum accuracy.
    3.4 Data to be entered into STORET must be reported as μg/1.
4. Precision and Accuracy
    4.1 A synthetic sample prepared by the Analytical Reference Service, PHS, containing 240 μg/1 B, 40 μg/1 As, 250 μg/1 Be, 20 μg/1 Se, and 6 μg/1 V in distilled water, was analyzed by the curcumin method with a relative standard deviation of 22.8% and a relative error of 0% in 30 laboratories.
5. Reference
    5.1 The procedure to be used for this determination is found in:
    Standard Methods for the Examination of Water and Wastewater, 13th Edition, p 69, Method 107A (1971).

BROMIDE

(Titrimetric)

STORET NO. 71870

1. Scope and Application
   1.1 This method is applicable to drinking, surface, and saline waters, domestic and industrial waste effluents.
   1.2 The concentration range for this method is 2-20 mg bromide/1.
2. Summary of Method
   2.1 After pretreatment to remove interferences, the sample is divided into two aliquots. One aliquot is analyzed for iodide by converting the iodide to iodate with bromine water and titrating iodometrically with phenylarsine oxide (PAO) or sodium thiosulfate. The other aliquot is analyzed for iodide plus bromide by converting these halides to iodate and bromate with calcium hypochlorite and titrating iodometrically with PAO or sodium thiosulfate. Bromide is then calculated by difference.
3. Sample Handling and Preservation
   3.1 Store at 4°C and analyze as soon as possible.
4. Interferences
   4.1 Iron, manganese and organic matter can interfere; however, the calcium oxide pretreatment removes or reduces these to insignificant concentrations.
   4.2 Color interferes with the observation of indicator and bromine-water color changes. This interference is eliminated by the use of a pH meter instead of a pH indicator and the use of standardized amounts of oxidant and oxidant-quencher.
5. Reagents
   5.1 Acetic Acid Solution (1:8): Mix 100 ml of glacial acetic acid with 800 ml of distilled water.
   5.2 Bromine Water: In a fume hood, add 0.2 ml bromine to 500 ml distilled water. Stir with a magnetic stirrer and a Teflon-coated stirring bar for several hours or until the bromine dissolves. Store in a glass-stoppered colored bottle.
   5.3 Calcium Carbonate ($CaCO_3$): Powdered
   5.4 Calcium Hypochlorite Solution ($Ca(OC1)_2$): Add 35 g of $Ca(OC1)_2$ to approximately 800 ml of distilled water in a 1 liter volumetric flask. Stir on a magnetic stirrer for approximately 30 minutes. Dilute to 1 liter and filter. Store in a glass-stoppered, colored flask.

5.5 Calcium Oxide (CaO): Anhydrous, powdered.

5.6 Hydrochloric Acid Solution (1:4): Mix 100 ml of HCl (sp. gr. 1.19) with 400 ml of distilled water.

5.7 Potassium Iodide (KI): Crystals, ACS Reagent Grade

5.8 Sodium Acetate Solution (275 g/1): Dissolve 275 g sodium acetate trihydrate ($NaC_2H_3O_2 \cdot 3H_2O$) in distilled water. Dilute to 1 liter and filter.

5.9 Sodium Chloride ($NaCl$): Crystals, ACS Reagent Grade

5.10 Sodium Formate Solution (500 g/1): Dissolve 50 g sodium formate ($NaCHO_2$) in hot distilled water and dilute to 100 ml.

5.11 Sodium Molybdate Solution (10 g/1): Dissolve 1 g sodium molybdate ($Na_2MoO_4 \cdot 2H_2O$) in distilled water and dilute to 100 ml.

5.12 Sulfuric Acid Solution (1:4): Slowly add 200 ml H_2SO_4 (sp. gr. 1.84) to 800 ml of distilled water.

5.13 Phenylarsine Oxide (0.0375N): Hach Chemical Co., or equivalent. Standardize with 0.0375 N potassium biiodate (5.19, 5.23).

5.14 Phenylarsine Oxide Working Standard (0.0075 N): Transfer 100 ml of commercially available 0.0375 N phenylarsine oxide (5.13) to a 500 ml volumetric flask and dilute to the mark with distilled water. This solution should be prepared fresh daily.

5.15 Amylose Indicator: Mallinckrodt Chemical Works or equivalent.

5.16 Sodium Thiosulfate, Stock Solution, 0.75 N: Dissolve 186.14 g $Na_2S_2O_3 \cdot 5H_2O$ in boiled and cooled distilled water and dilute to 1 liter. Preserve by adding 5 ml chloroform.

5.17 Sodium Thiosulfate Standard Titrant, 0.0375 N: Prepare by diluting 50.0 ml of stock solution (5.16) to 1.0 liter. Preserve by adding 5 ml of chloroform. Standardize with 0.0375 N potassium biiodate (5.19, or 5.23).

5.18 Sodium Thiosulfate Working Standard (0.0075 N): Transfer 100 ml of sodium thiosulfate standard titrant (5.17) to a 500 ml volumetric flask and dilute to the mark with distilled water. This solution should be prepared fresh daily.

5.19 Potassium Biiodate Standard, 0.0375 N: Dissolve 4.873 g potassium biiodate, previously dried 2 hours at 103°C, in distilled water and dilute to 1.0 liter. Dilute 250 ml to 1.0 liter for 0.0375 N biiodate solution.

5.20 Starch Solution: Prepare an emulsion of 10 g of soluble starch in a mortar or beaker with a small quantity of distilled water. Pour this emulsion into 1 liter of boiling water, allow to boil a few minutes, and let settle overnight. Use the clear supernate. This solution may be preserved by the addition of 5 ml per liter of chloroform and storage in a 10°C refrigerator. Commercially available dry, powdered starch indicators may be used in place of starch solution.

5.21 Nitrogen Gas: Cylinder

5.22 Potassium Fluoride ($KF \cdot 2H_2O$): ACS Reagent Grade

5.23 Standardization of 0.0375 N Phenylarsine Oxide and 0.0375 N Sodium Thiosulfate: Dissolve approximately 2 g (±1.0 g) KI (5.7) in 100 to 150 ml distilled water; add 10 ml H_2SO_4 solution (5.12) followed by 20 ml standard potassium biiodate solution (5.19). Place in dark for 5 minutes, dilute to 300 ml and titrate with the phenylarsine oxide (5.13) or sodium thiosulfate (5.17) to a pale straw color. Add a small scoop of indicator (5.15). Wait until homogeneous blue color develops and continue the titration drop by drop until the color disappears. Run in duplicate. Duplicate determinations should agree within ±0.05 ml.

6. Procedure

6.1 Pretreatment

6.1.1 Add a visible excess of CaO (5.5) to 400 ml of sample. Stir or shake vigorously for approximately 5 minutes. Filter through a dry, moderately retentive filter paper, discarding the first 75 ml.

6.2 Iodide Determination

6.2.1 Place 100 ml of pretreated sample (6.1) or a fraction thereof diluted to that volume, into a 150 ml beaker. Add a Teflon-coated stirring bar and place on a magnetic stirrer. Insert a pH electrode and adjust the pH to approximately 7 or slightly less by the dropwise addition of H_2SO_4 solution (5.12).

6.2.2 Transfer the sample to a 250 ml widemouthed conical flask. Wash beaker with small amounts of distilled water and add washings to the flask. A 250 ml iodine flask would increase accuracy and precision by preventing possible loss of the iodine generated upon addition of potassium iodide and sulfuric acid (6.4.1).

6.2.3 Add 15 ml sodium acetate solution (5.8) and 5 ml acetic acid solution (5.1). Mix well. Add 40 ml bromine water solution (5.2); mix well. Wait 5 minutes.

6.2.4 Add 2 ml sodium formate solution (5.10); mix well. Wait 5 minutes.

6.2.5 Purge space above sample with gentle stream of nitrogen (5.21) for approximately 30 seconds to remove bromine fumes.

6.2.6 If a precipitate forms (iron), add 0.5 g $KF \cdot 2H_2O$ (5.22).

6.2.7 A distilled water blank must be run with each set of samples because of iodide in reagents. If the blank is consistently shown to be zero for a particular "lot" of chemicals, it can be ignored.

6.2.8 Proceed to step (6.4).

6.3 Bromide Plus Iodide Determination

6.3.1 Place 100 ml of pretreated sample (6.1) or a fraction thereof diluted to that volume, in a 150 ml beaker. Add 5 g NaCl and stir to dissolve. Neutralize by dropwise addition of HCl solution (5.6) as in (6.2.1). Transfer as in (6.2.2).

6.3.2 Add 20 ml of calcium hypochlorite solution (5.4). Add 1 ml of HCl solution (5.6) and add approximately 0.2 g calcium carbonate (5.3).

6.3.3 Heat to boiling on a hot plate; maintain boiling for 8 minutes.

6.3.4 Remove from hot plate and carefully add 4 ml sodium formate solution (5.10). *Caution: TOO RAPID ADDITION MAY CAUSE FOAMING.* Wash down sides with distilled water.

6.3.5 Return to hot plate and maintain boiling conditions for an additional 8 minutes. Occasionally wash down sides with distilled water if residue is deposited from boiling action.

6.3.6 Remove from hot plate. Wash down sides and allow to cool.

6.3.7 If a precipitate forms (iron), add 0.5 g $KF \cdot 2H_2O$ (5.22).

6.3.8 Add 3 drops sodium molybdate solution (5.11).

6.3.9 A distilled water blank must be run with each set of samples because of iodide, iodate, bromide, and/or bromate in reagents.

6.3.10 Proceed to step (6.4).

6.4 Titration

6.4.1 Dissolve approximately 1 g potassium iodide (5.7) in sample from (6.2.8 or 6.3.10). Add 10 ml of H_2SO_4 solution (5.12) and place in dark for 5 minutes.

6.4.2 Titrate with standardized phenylarsine oxide working standard (5.14) or sodium thiosulfate working standard (5.18), adding indicator (5.15, or 5.20) as end point is approached (light straw color). Titrate to colorless solution. Disregard returning blue color.

7. Calculations

7.1 Principle: Iodide is determined by the titration of the sample as oxidized in (6.2): bromide plus iodide is determined by the titration of the sample as oxidized in (6.3). The amount of bromide is then determined by difference. The number of equivalents of iodine produced a constant of 13,320 as shown in the equation in (7.2). Experimental data is entered in the appropriate place and the equation is solved for mg/l bromide.

7.2 Equation

$$\mathrm{Br(mg/l)} = 13{,}320 \left[\left(\frac{A \times B}{C} \right) - \left(\frac{D \times E}{F} \right) \right]$$

where

A = the number of ml of PAO needed to titrate the sample for bromide plus iodide (with the number of ml of PAO needed to titrate the blank subtracted).

B = the normality of the PAO needed to titrate the sample for bromide plus iodide

C = the volume of sample taken (100 ml or a fraction thereof) to be titrated for bromide plus iodide.

D = the number of ml of PAO needed to titrate the sample for iodide (with the number of ml of PAO needed to titrate the blank subtracted). The blank for the iodide titration is often zero.

E = the normality of the PAO used to titrate the sample for iodide.

F = the volume of sample taken (100 ml or a fraction thereof) to be titrated for iodide.

8. Precision and Accuracy

8.1 In a single laboratory (MDQARL), using a mixed domestic and industrial waste effluent, at concentrations of 0.3, 2.8, 5.3, 10.3 and 20.3 mg/l of bromide, the standard deviations were ±0.13, ±0.37, ±0.38, ±0.44 and ±0.42 mg/l, respectively.

8.2 In a single laboratory (MDQARL), using a mixed domestic and industrial waste effluent, at concentrations of 2.8, 5.3, 10.3 and 20.3 mg/l of bromide, recoveries were 96, 83, 97 and 99%, respectively.

Bibliography

1. ASTM Standards, Part 23, Water; Atmospheric Analysis, p 331-333, Method D1246-C (1973).

CALCIUM

STORET NO. Calcium (mg/l $CaCO_3$) 00910
Calcium, Total (mg/l Ca) 00916

1. Scope and Application
   1.1 This method is applicable to drinking and surface waters, domestic and industrial wastes.
   1.2 The lower detection limit of this method is approximately 0.5 mg/l as $CaCO_3$; the upper limit can be extended to all concentrations by sample dilution. It is recommended that a sample aliquot containing not more than 25 mg $CaCO_3$ be used.
2. Summary of Method
   2.1 Calcium ion is sequestered upon the addition of disodium dihydrogen ethylenediamine tetraacetate (EDTA). The titration end point is detected by means of an indicator which combines with calcium only.
3. Interferences
   3.1 Strontium and barium interfere and alkalinity in excess of 30 mg/l may cause an indistinct end point. Magnesium interference is reduced or eliminated by raising the pH between 12-13 to precipitate magnesium hydroxide.
4. Precision and Accuracy
   4.1 A synthetic unknown sample containing 108 mg/l Ca, 82 mg/l Mg, 3.1 mg/l K, 19.9 mg/l Na, 241 mg/l chloride, 1.1 mg/l nitrate N, 250 μg/l nitrite N, 259 mg/l sulfate, and 42.5 mg/l total alkalinity in distilled water was determined by this method with a relative standard deviation of 9.2% and a relative error of 1.9% in 44 laboratories.
5. Reference
   5.1 The procedure to be used for this determination is found in: Standard Methods for the Examination of Water and Wastewater, 13th Edition, p 84, Method 110C (1971).

CHEMICAL OXYGEN DEMAND

STORET NO. 00340

1. Scope and Application

   1.1 The Chemical Oxygen Demand (COD) method determines the quantity of oxygen required to oxidize the organic matter in a waste sample, under specific conditions of oxidizing agent, temperature, and time.

   1.2 Since the test utilizes a rigorous chemical oxidation rather than a biological process, the result has no defineable relationship to the Biochemical Oxygen Demand (BOD) of the waste. The test result should be considered as an independent measurement of organic matter in the sample, rather than as a substitute for the BOD test.

   1.3 The method can be applied to domestic and industrial waste samples having an organic carbon concentration greater than 15 mg/1. For lower concentrations of carbon such as in surface water samples, the Low Level Modification should be used. When the chloride concentration of the sample exceeds 2000 mg/1, the modification for saline waters is required.

2. Summary of Method

   2.1 Organic substances in the sample are oxidized by potassium dichromate in 50% sulfuric acid solution at reflux temperature. Silver sulfate is used as a catalyst and mercuric sulfate is added to remove chloride interference. The excess dichromate is titrated with standard ferrous ammonium sulfate, using orthophenanthroline ferrous complex as an indicator.

3. Comments

   3.1 To reduce loss of volatile organics, the flask should be cooled during addition of the sulfuric acid solution.

4. Precision and Accuracy

   4.1 Eighty-six analysts in fifty-eight laboratories analyzed a distilled water solution containing oxidizable organic material equivalent to 270 mg/1 COD. The standard deviation was ±17.76 mg/l COD with an accuracy as percent relative error (bias) of -4.7%. (EPA Method Research Study 3).

5. References

   5.1 The procedure to be used for this determination is found in:

   Standard Methods for the Examination of Water and Wastewater, 13th Edition, p 495, Method 220 (1971).

   ASTM Standards, Part 23, Water; Atmospheric Analysis, p 470, Method D 1252-67 (1973).

CHEMICAL OXYGEN DEMAND

(Low Level)

STORET NO. 00335

1. Scope and Application

1.1 The scope of this modification of the Chemical Oxygen Demand (COD) test is the same as for the high level test. It is applicable to the analysis of surface waters, domestic and industrial wastes with low demand characteristics.

1.2 This method (low level) is applicable for samples having a COD in the range of 5-50 mg/1 COD.

2. Summary of Method

2.1 Organic and oxidizable inorganic substances in an aqueous sample are oxidized by potassium dichromate solution in 50 percent (by volume) sulfuric acid in solution. The excess dichromate is titrated with standard ferrous ammonium sulfate using orthophenanthroline ferrous complex (ferroin) as an indicator.

3. Sampling and Preservation

3.1 Collect the samples in glass bottles, if possible. Use of plastic containers is permissible if it is known that no organic contaminants are present in the containers.

3.2 Biologically active samples should be tested as soon as possible. Samples containing settleable material should be well mixed, preferably homogenized, to permit removal of representative aliquots.

3.3 Samples may be preserved with sulfuric acid at a rate of 2 ml of conc. H_2SO_4 per liter of sample.

4. Interferences

4.1 Traces of organic material either from the glassware or atmosphere may cause a gross, positive error.

4.1.1 Extreme care should be exercised to avoid inclusion of organic materials in the distilled water used for reagent preparation or sample dilution.

4.1.2 Glassware used in the test should be conditioned by running blank procedures to eliminate traces of organic material.

4.2 Volatile materials may be lost when the sample temperature rises during the sulfuric acid addition step.

4.3 Chlorides are quantitatively oxidized by dichromate and represent a positive interference. Mercuric sulfate is added to the digestion flask to complex the chlorides, thereby effectively eliminating the interference on all but brine and estuarine samples.

5. Apparatus

5.1 Reflux apparatus: Glassware should consist of a 500 ml Erlenmeyer flask or a 300 ml round bottom flask made of heat-resistant glass connected to a 12 inch Allihn condenser by means of a ground glass joint. Any equivalent reflux apparatus may be substituted provided that a ground-glass connection is used between the flask and the condenser.

6. Reagents

6.1 Distilled water: Special precautions should be taken to insure that distilled water used in this test be low in organic matter.

6.2 Standard potassium dichromate solution (0.025 N): Dissolve 12.259 g $K_2Cr_2O_7$, primary standard grade, previously dried at 103°C for two hours, in distilled water and dilute to 1000 ml. Mix this solution thoroughly then dilute 100.0 ml to 1000 ml with distilled water.

6.3 Sulfuric acid reagent: Conc. H_2SO_4 containing 23.5 g silver sulfate, Ag_2SO_4, per 9 lb. bottle. (With continuous stirring, the silver sulfate may be dissolved in about 30 minutes.)

6.4 Standard ferrous ammonium sulfate (0.025 N): Dissolve 98 g of $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ in distilled water. Add 20 ml of conc. H_2SO_4 (6.8), cool and dilute to 1 liter. Dilute 100 ml of this solution to 1 liter with distilled water. This solution must be standardized daily against $K_2Cr_2O_7$ solution.

6.4.1 Standardization: To 15 ml of distilled water add 10.0 ml of 0.025 N $K_2Cr_2O_7$ (6.2) solution. Add 20 ml of H_2SO_4 (6.8) and cool. Titrate with ferrous ammonium sulfate (6.4) using 1 drop of ferroin indicator (6.6). The color change is sharp, going from blue-green to reddish-brown.

$$\text{Normality} = \frac{(\text{ml } K_2Cr_2O_7)\ (0.025)}{\text{ml Fe } (NH_4)_2\ (SO_4)_2}$$

6.5 Mercuric sulfate : Powdered $HgSO_4$.

6.6 Phenanthroline ferrous sulfate (ferroin) indicator solution: Dissolve 1.48 g of 1-10 (ortho)phenanthroline monohydrate, together with 0.70 g of $FeSO_4 \cdot 7H_2O$ in 100 ml of water. This indicator may be purchased already prepared.

6.7 Silver sulfate : Powdered Ag_2SO_4.

6.8 Sulfuric acid (sp. gr. 1.84) : Concentrated H_2SO_4.

7. Procedure

7.1 Place several boiling stones in the reflux flask, followed by 1 g of $HgSO_4$ (6.5). Add 5.0 ml conc. H_2SO_4 (6.8); swirl until mercuric sulfate has dissolved. Place reflux flask in an ice bath and slowly add, with swirling, 25.0 ml of 0.025 N $K_2Cr_2O_7$ (6.2). Now add 70 ml of sulfuric acid-silver sulfate solution (6.3) to the cooled reflux flask, again using slow addition with swirling motion.

7.2 With the reflux flask still in the ice bath, place 50.0 ml of sample or an aliquot diluted to 50.0 ml into the reflux flask.

Caution: Care must be taken to assure that the contents of the flask are well mixed. If not, superheating may result, and the mixture may be blown out of the open end of the condenser. Attach the flask to the condenser and start the cooling water.

7.3 Apply heat to the flask and reflux for 2 hours. For some waste waters, the 2-hour reflux period is not necessary. The time required to give the maximum oxidation for a wastewater of constant or known composition may be determined and a shorter period of refluxing may be permissible.

7.4 Allow the flask to cool and wash down the condenser with about 25 ml of distilled water. If a round bottom flask has been used, transfer the mixture to a 500 ml Erlenmeyer flask, washing out the reflux flask 3 or 4 times with distilled water. Dilute the acid solution to about 300 ml with distilled water and allow the solution to cool to about room temperature. Add 8 to 10 drops of ferroin indicator (6.6) to the solution and titrate the excess dichromate with 0.025 N ferrous ammonium sulfate (6.4) solution to the end point. The color change will be sharp, changing from a blue-green to a reddish hue.

7.5 Blank – Simultaneously run a blank determination following the details given in (7.1) and (7.2), but using low COD water in place of sample.

8. Calculation

8.1 Calculate the COD in the sample in mg/1 as follows:

$$\text{COD, mg/liter} = \frac{(A\text{-}B)N \times 8000}{S}$$

where

A = milliliters of $Fe(NH_4)_2(SO_4)_2$ solution required for titration of the blank,

B = milliliters of $Fe(NH_4)_2(SO_4)_2$ solution required for titration of the sample,

N = normality of the $Fe(NH_4)_2(SO_4)_2$ solution, and

S = milliliters of sample used for the test.

9. Precision and Accuracy

9.1 Eighty-six analysts in fifty-eight laboratories analyzed a distilled water solution containing oxidizable organic material equivalent to 12.3 mg/l COD. The standard deviation was ±4.15 mg/l COD with an accuracy as percent relative error (bias) of 0.3%. (EPA Method Research Study 3.)

CHEMICAL OXYGEN DEMAND

(High Level for Saline Waters)

STORET NO. 00340

1. Scope and Application

   1.1 When the chloride level exceeds 1000 mg/1 the minimum accepted value for the COD will be 250 mg/1. COD levels which fall below this value are highly questionable because of the high chloride correction which must be made.

2. Summary of Method

   2.1 Organic and oxidizable inorganic substances in an aqueous sample are oxidized by potassium dichromate solution in 50 percent (by volume) sulfuric acid solution. The excess dichromate is titrated with standard ferrous ammonium sulfate using orthophenanthroline ferrous complex (ferroin) as an indicator.

3. Sample Handling and Preservation

   3.1 Collect the samples in glass bottles, if possible. Use of plastic containers is permissible if it is known that no organic contaminants are present in the containers.

   3.2 Biologically active samples should be tested as soon as possible. Samples containing settleable material should be well mixed, preferably homogenized, to permit removal of representative aliquots.

   3.3 Samples are preserved by the addition of 2 ml of conc. H_2SO_4 per liter of sample.

4. Interferences

   4.1 Traces of organic material either from the glassware or atmosphere may cause a gross, positive error.

      4.1.1 Extreme care should be exercised to avoid inclusion of organic materials in the distilled water used for reagent preparation or sample dilution.

      4.1.2 Glassware used in the test should be conditioned by running blank procedures to eliminate traces of organic material.

   4.2 Volatile materials may be lost when the sample temperature rises during the sulfuric acid addition step.

   4.3 Chlorides are quantitatively oxidized by dichromate and represent a positive interference. Mercuric sulfate is added to the digestion flask to complex the chlorides, thereby effectively eliminating the interference on all but brine samples.

5. Apparatus

5.1 Reflux apparatus: Glassware should consist of a 500 ml Erlenmeyer flask or a 300 ml round bottom flask made of heat-resistant glass connected to a 12 inch Allihn condenser by means of a ground glass joint. Any equivalent reflux apparatus may be substituted provided that a ground-glass connection is used between the flask and the condenser.

6. Reagents

6.1 Standard potassium dichromate solution, (0.25 N): Dissolve 12.2588 g of $K_2Cr_2O_7$, primary standard grade, previously dried for 2 hours at 103°C in water and dilute to 1000 ml.

6.2 Sulfuric acid reagent: Conc. H_2SO_4 containing 23.5 g silver sulfate, Ag_2SO_4, per 9 lb. bottle. (With continuous stirring, the silver sulfate may be dissolved in about 30 minutes.)

6.3 Standard ferrous ammonium sulfate, 0.250 N; Dissolve 98 g of $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ in distilled water. Add 20 ml of conc. H_2SO_4, (6.7), cool and dilute to 1 liter. This solution must be standardized against the standard potassium dichromate solution (6.1) daily.

6.3.1 Standardization: Dilute 25.0 ml of standard dichromate solution (6.1) to about 250 ml with distilled water. Add 75 ml conc. sulfuric acid (6.7). Cool, then titrate with ferrous ammonium sulfate titrant (6.3), using 10 drops of ferroin indicator (6.5).

$$\text{Normality} = \frac{(\text{ml } K_2Cr_2O_7)(0.25)}{\text{ml Fe } (NH_4)_2\ (SO_4)_2}$$

6.4 Mercuric sulfate : Powdered $HgSO_4$.

6.5 Phenanthroline ferrous sulfate (ferroin) indicator solution: Dissolve 1.48 g of 1-10-(ortho)-phenanthroline monohydrate, together with 0.70 g of $FeSO_4 \cdot 7H_2O$ in 100 ml of water. This indicator may be purchased already prepared.

6.6 Silver sulfate : Powdered Ag_2SO_4.

6.7 Sulfuric acid (sp. gr. 1.84) : Concentrated H_2SO_4.

7. Procedure

7.1 Pipet a 50.0 ml aliquot of sample not to exceed 800 mg/1 of COD into a 500 ml, flat bottom, Erlenmeyer flask. Add 25.0 ml of 0.25 N $K_2Cr_2O_7$ (6.1), then 5 ml of conc. H_2SO_4 (6.7). Add $HgSO_4$ (6.4) in the ratio of 10 mg to 1 mg chloride, based upon the mg of chloride in the sample aliquot. Swirl until all the mercuric sulfate has dissolved. Carefully add 70 ml of sulfuric acid-silver sulfate solution

(6.2) and gently swirl until the solution is thoroughly mixed. Glass beads should be added to the reflux mixture to prevent bumping, which can be severe and dangerous.

Caution: The reflux mixture must be thoroughly mixed before heat is applied. If this is not done, local heating occurs in the bottom of the flask, and the mixture may be blown out of the condenser.

7.1.1 If volatile organics are present in the sample, use an Allihn condenser and add the sulfuric acid-silver sulfate solution through the condenser, while cooling the flask, to reduce loss by volatilization.

7.2 Attach the flask to the condenser and reflux the mixture for two hours.

7.3 Cool, and wash down the interior of the condenser with 25 ml of distilled water. Disconnect the condenser and wash the flask and condenser joint with 25 ml of distilled water so that the total volume is 350 ml. Cool to room temperature.

7.4 Titrate with standard ferrous ammonium sulfate (6.3) using 10 drops of ferroin (6.5) indicator. (This amount must not vary from blank, sample and standardization). The color change is sharp, going from blue-green to reddish-brown and should be taken as the end point although the blue-green color may reappear within minutes.

7.5 Run a blank, using 50 ml of distilled water in place of the sample together with all reagents and subsequent treatment.

7.6 For COD values greater than 800 mg/1, a smaller aliquot of sample should be taken; however, the volume should be readjusted to 50 ml with distilled water having a chloride concentration equal to the sample.

7.7 Chloride correction (1): Prepare a standard curve of COD versus mg/1 of chloride, using sodium chloride solutions of varying concentrations following exactly the procedure outlined. The chloride interval, as a minimum should be 4000 mg/l up to 20,000 mg/1 chloride. Lesser intervals of greater concentrations must be run as per the requirements of the data, but in no case must extrapolation be used.

8. Calculation

8.1 $$\text{mg/1 COD} = \frac{[(A\text{-}B)\, C \times 8{,}000] - 50D}{\text{ml sample}} \times 1.2$$

Where:

COD = chemical oxygen demand from dichromate

A = ml $Fe\,(NH_4)_2\,(SO_4)_2$ for blank;

B = ml $Fe\,(NH_4)_2\,(SO_4)_2$ for sample;

C = normality of Fe $(NH_4)_2(SO_4)_2$;

D = chloride correction from curve (step 7.7)

1.2 = compensation factor to account for the extent of chloride oxidation which is dissimilar in systems containing organic and non-organic material.

9. Precision and Accuracy.

9.1 Precision and accuracy data are not available at this time.

Bibliography

1. Burns, E. R., Marshall, C., Journal WPCF, Vol. 37, p 1716-1721 (1965).

CHLORIDE

STORET NO. 00940

1. Scope and Application
   1.1 This method is applicable to drinking, surface, and saline waters, domestic and industrial wastes.
   1.2 The method is suitable for all concentration ranges of chloride content; however, in order to avoid large titration volumes, use a sample aliquot containing not more than 10 to 20 mg Cl per 50 ml.
   1.3 Automated titration may be used.
2. Summary of Method
   2.1 Dilute mercuric nitrate solution is added to an acidified sample in the presence of mixed diphenylcarbazone-bromophenol blue indicator. The end point of the titration is the formation of the blue-violet mercury diphenylcarbazone complex.
3. Comments
   3.1 Anions and cations at concentrations normally found in surface waters do not interfere.
   3.2 Sulfites interfere. If presence is suspected, oxidize by treating 50 ml of sample with 0.5 to 1 ml of H_2O_2.
4. Precision and Accuracy
   4.1 Forty-two analysts in eighteen laboratories analyzed synthetic water samples containing exact increments of chloride, with the following results:

Increment as Chloride mg/liter	Precision as Standard Deviation mg/liter	Accuracy as	
		Bias, %	Bias, mg/liter
17	1.54	+2.16	+0.4
18	1.32	+3.50	+0.6
91	2.92	+0.11	+0.1
97	3.16	- 0.51	- 0.5
382	11.70	- 0.61	- 2.3
398	11.80	- 1.19	- 4.7

(FWPCA Method Study 1, Mineral and Physical Analyses)

4.2 In a single laboratory (MDQARL), using surface water samples at an average concentration of 34 mg Cl/l, the standard deviation was ±1.0.

5. Reference

5.1 The procedure to be used for this determination is found in:

ASTM Standards, Part 23, Water; Atmospheric Analysis, p 273, Method 512-67, Referee Method A (1973).

CHLORIDE
(Automated)

STORET NO. 00940

1. Scope and Application
   1.1 This automated method is applicable to drinking, surface, and saline waters, domestic and industrial wastes. The applicable range is 1 to 250 mg Cl/1. Approximately 15 samples per hour can be analyzed.
2. Summary of Method
   .2.1 Thiocyanate ion (SCN) is liberated from mercuric thiocyanate, through sequestration of mercury by chloride ion to form un-ionized mercuric chloride. In the presence of ferric ion, the liberated SCN forms highly colored ferric thiocyanate, in concentration proportional to the original chloride concentration.
3. Sample Handling and Preservation
   3.1 No special requirements.
4. Interferences
   4.1 No significant interferences.
5. Apparatus
   5.1 Technicon AutoAnalyzer consisting of:
      5.1.1 Sampler I.
      5.1.2 Continuous filter.
      5.1.3 Manifold.
      5.1.4 Proportioning pump.
      5.1.5 Colorimeter equipped with 15 mm tubular flow cell and 480 nm filters.
      5.1.6 Recorder.
6. Reagents
   6.1 Ferric Ammonium Sulfate: Dissolve 60 g of $FeNH_4(SO_4)_2 \cdot 12H_2O$ in approximately 500 ml distilled water. Add 355 ml of conc. HNO_3 and dilute to 1 liter with distilled water. Filter.
   6.2 Saturated Mercuric Thiocyanate: Dissolve 5 g of $Hg(SCN)_2$ in 1 liter of distilled water. Decant and filter a portion of the saturated supernatant liquid to use as the reagent and refill the bottle with distilled water.
   6.3 Stock Solution (0.0141 N NaCl): Dissolve 0.8241 g of pre-dried (140°C) NaCl in distilled water. Dilute to 1 liter in a volumetric flask. 1 ml = 0.5 mg Cl.

6.3.1 Prepare a series of standards by diluting suitable volumes of stock solution to 100.0 ml with distilled water. The following dilutions are suggested:

ml of Stock Solution	Conc., mg/l
1.0	5.0
2.0	10.0
4.0	20.0
8.0	40.0
15.0	75.0
20.0	100.0
30.0	150.0
40.0	200.0
50.0	250.0

7. Procedure

7.1 No advance sample preparation is required. Set up manifold as shown in Figure 1. For water samples known to be consistently low in chloride content, it is advisable to use only one distilled water intake line.

7.2 Allow both colorimeter and recorder to warm up for 30 minutes. Run a baseline with all reagents, feeding distilled water through the sample line. Adjust dark current and operative opening on colorimeter to obtain stable baseline.

7.3 Place distilled water wash tubes in alternate openings in sampler and set sample timing at 2.0 minutes.

7.4 Place working standards in sampler in order of decreasing concentrations. Complete filling of sampler tray with unknown samples.

7.5 Switch sample line from distilled water to sampler and begin analysis.

8. Calculation

8.1 Prepare standard curve by plotting peak heights of processed standards against known concentrations. Compute concentration of samples by comparing sample peak heights with standard curve.

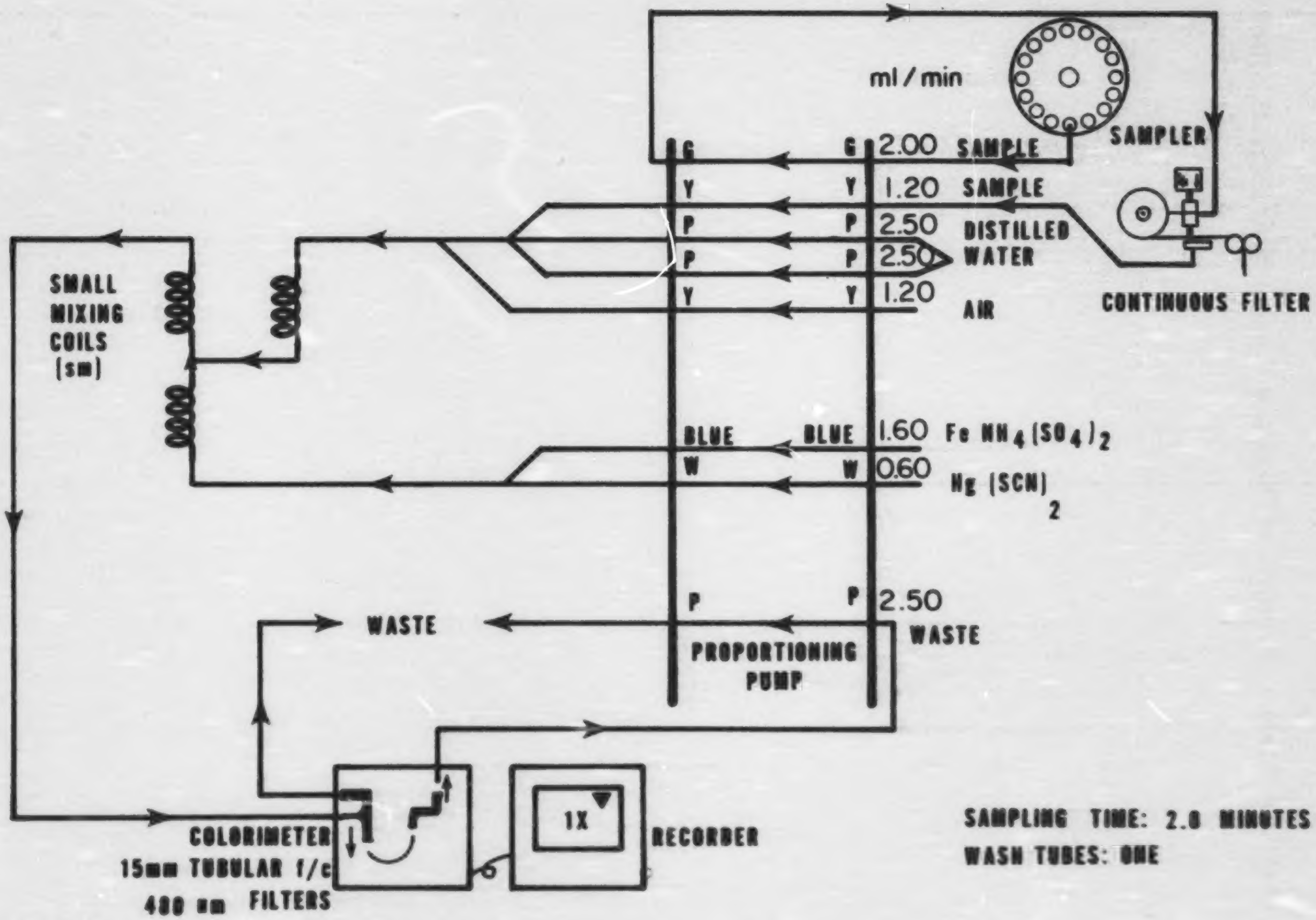
9. Precision and Accuracy

9.1 In a single laboratory (MDQARL), using surface water samples at concentrations of 1, 100, and 250 mg Cl/l, the standard deviation was ±0.3.

9.2 In a single laboratory (MDQARL), using surface water samples at concentrations of 10 and 100 mg Cl/l, recoveries were 97% and 104%, respectively.

Bibliography

1. J. E. O'Brien, "Automatic Analysis of Chlorides in Sewage," Waste Engr., 33, 670-672 (Dec. 1962).


ml / min
SAMPLER
G
G
2.00
SAMPLE
Y
Y
1.20
SAMPLE
P
P
2.50
DISTILLED WATER
P
P
2.50
Y
Y
1.20
AIR
CONTINUOUS FILTER
SMALL MIXING COILS (sm)
BLUE
BLUE
1.60
Fe NH4 (SO4)2
W
W
0.60
Hg (SCN) 2
P
P
2.50
WASTE
WASTE
PROPORTIONING PUMP
COLORIMETER
15mm TUBULAR f/c
400 nm FILTERS
1X
RECORDER

SAMPLING TIME: 2.0 MINUTES
WASH TUBES: ONE

FIGURE 1. CHLORIDE MANIFOLD AA-I

CHLORINE, Total Residual

STORET NO. 50060

1. Scope and Application

   1.1 The Amperometric Titration method is applicable to all types of waters and wastes that do not contain a substantial amount of organic matter. This method cannot be used for samples containing above 5 mg/1 total residual chlorine.

2. Summary of Method

   2.1 Phenylarsine oxide is titrated into a buffered sample contained in an amperometric titration cell until the generation of current ceases. Potassium iodide is added when chlorine is present as a chloramine.

   2.2 In the iodometric titration, chlorine liberates free iodine from potassium iodide solutions when its pH is 8 or less. The liberated iodine is titrated with a standard solution of sodium thiosulfate or phenylarsine oxide with starch as an indicator. NOTE: In a sewage or other wastewater sample containing a substantial amount of organic matter, excess sodium thiosulfate or PAO is titrated with a standard iodine solution until the thiosulfate or PAO is completely oxidized.

3. Interferences

   3.1 Samples containing significant amounts of organic matter interfere with the amperometric titration and the iodometric method must be used.

   3.2 The amperometric titration is not subject to interference from color, turbidity, iron, manganese, or nitrite nitrogen.

4. Sample Handling and Preservation

   4.1 Chlorine determinations must be started immediately after sampling, avoiding excessive light and agitation. Samples to be analyzed for chlorine cannot be stored.

5. Reference

   5.1 The procedure to be used for this determination is found in:
   Standard Methods for the Examination of Water and wastewater, 13th Edition, p 382, Method 204A (1971).
   ASTM Standards, Part 23, Water; Atmospheric Analysis, p 280, Method D1253-68 (1973).

COLOR

(Platinum-Cobalt)

STORET NO. 00080

1. Scope and Application

1.1 The Platinum-Cobalt method is useful for measuring color of water derived from naturally occurring materials, i.e., vegetable residues such as leaves, barks, roots, humus and peat materials. *The method is not applicable to color measurement on waters containing highly colored industrial wastes.*

NOTE 1: The Spectrophotometric and Tristimulus methods are useful for detecting specific color problems. The use of these methods, however, is laborious and unless determination of the hue, purity, and luminance is desired, they are of limited value.

2. Summary of Method

2.1 Color is measured by visual comparison of the sample with platinum-cobalt standards. One unit of color is that produced by 1 mg/1 platinum in the form of the chloroplatinate ion.

3. Interferences

3.1 Since very slight amounts of turbidity interfere with the determination, samples showing visible turbidity should be clarified by centrifugation.

3.2 Method is pH dependent.

4. Sample Handling and Preservation

4.1 Representative samples shall be taken in scrupulously clean glassware.

4.2 Since biological activity may change the color characteristics of a sample, the determination should be made as soon as possible. Refrigeration at 4°C is recommended.

5. Apparatus

5.1 Nessler tubes : Matched, tall form, 50 ml capacity.

6. Reagents

6.1 Standard chloroplatinate solution: Dissolve 1.246 g potassium chlorplatinate, K_2PtCl_6, (equivalent to 0.500 g metallic Pt) and 1 g crystalline cobaltous chloride, $CoCl_2 \cdot 6H_2O$, in distilled water containing 100 ml of conc. HCl. Dilute to 1000 ml with distilled water. This standard solution is equivalent to 500 color units.

7. Preparation of Standards

7.1 Prepare standards in increments from 5 to 70 units. The following series is suggested:

ml of Standard Solution Diluted to 50.0 ml with Distilled Water	Color in Chloroplatinate Units
0.0	0
0.5	5
1.0	10
1.5	15
2.0	20
2.5	25
3.0	30
3.5	35
4.0	40
4.5	45
5.0	50
6.0	60
7.0	70

7.2 Protect these standards against evaporation and contamination by use of clean, inert stoppers.

NOTE 2: The standards also must be protected against the absorption of ammonia since an increase in color will result.

8. Procedure

8.1 Apparent color: Observe the color of the sample by filling a matched Nessler tube to the 50 ml mark with the water and compare with standards. This comparison is made by looking vertically downward through the tubes toward a white or specular surface placed at such an angle that light is reflected upward through the columns of liquid. If turbidity has not been removed by the procedure given in (8.2), report the color as "apparent color". If the color exceeds 70 units, dilute the sample with distilled water in known proportions until the color is within the range of the standards.

8.2 True color: Remove turbidity by centrifuging the sample until the supernatant is clear. The time required will depend upon the nature of the sample, the speed of the motor, and the radius of the centrifuge, but rarely will more than one hour be necessary. Compare the centrifuged sample with distilled water to insure that turbidity has been removed. If the sample is clear, then compare with standards as given in (8.1).

9. Calculation

9.1 Calculate the color units by means of the following equation:

$$\text{Color units} = \frac{A \times 50}{V}$$

where:

A = estimated color of diluted sample.
V = ml sample taken for dilution.

9.2 Report the results in whole numbers as follows:

Color Units	Record to Nearest
1-50	1
51-100	5
101-250	10
251-500	20

10. Precision and Accuracy

10.1 Precision and accuracy data are not available at this time.

11. Reference

11.1 The procedure to be used for this determination is found in:

Standard Methods for the Examination of Water and Wastewater, 13th Edition, p 160, Method 118 (1971).

COLOR
(Spectrophotometric)

STORET NO. 00080

1. Scope and Application
    1.1 This method is applicable to drinking, surface, and saline waters, domestic and industrial wastes. It must be used for industrial wastes that cannot be determined by the Platinum-Cobalt method.
2. Summary of Method
    2.1 Color characteristics are measured at pH 7.6 and at the original pH by obtaining the visible absorption spectrum of the sample on a spectrophotometer. The percent transmission at certain selected wavelengths is used to calculate the results.
    2.2 The results are expressed in terms of dominant wavelength, hue, luminance, and purity.
3. Interferences
    3.1 Since very slight amounts of turbidity interfere with the determination, samples must be filtered before analysis.
4. Sample Handling and Preservation
    4.1 Since biological activity may change the color characteristics of a sample, the determination should be made as soon as possible. Refrigeration at 4°C is recommended.
5. Reference
    5.1 The procedure to be used for this determinationis found in:
    Standard Methods for the Examination of Water and Wastewater, 13th Edition, p 391, Method 206A (1971).

CYANIDE, Total

STORET NO. 00720

1. Scope and Application
   1.1 This method is applicable to the determination of cyanide in drinking, surface, and saline waters, domestic and industrial wastes.
   1.2 The titration procedure using silver nitrate with p-dimethylamino-benzalrhodanine indicator is used for measuring concentrations of cyanide exceeding 1 mg/1 (0.2 mg/200 ml of absorbing liquid).
   1.3 The colorimetric procedure is used for concentrations below 1 mg/1 of cyanide and is sensitive to about 0.02 mg/1.
2. Summary of Method
   2.1 The cyanide as hydrocyanic acid (HCN) is released from cyanide complexes by means of a reflux-distillation operation and absorbed in a scrubber containing sodium hydroxide solution. The cyanide ion in the absorbing solution is then determined by volumetric titration or colorimetrically.
   2.2 In the colorimetric measurement the cyanide is converted to cyanogen chloride, CNCl, by reaction with chloramine-T at a pH less than 8 without hydrolyzing to the cyanate. After the reaction is complete, color is formed on the addition of pyridine-pyrazolone or pyridine-barbituric acid reagent. The absorbance is read at 620 nm when using pyridine-pyrazolone or 578 nm for pyridine-barbituric acid. To obtain colors of comparable intensity, it is essential to have the same salt content in both the sample and the standards.
   2.3 The titrimetric measurement uses a standard solution of silver nitrate to titrate cyanide in the presence of a silver sensitive indicator.
3. Definitions
   3.1 Cyanide is defined as cyanide ion and complex cyanides converted to hydrocyanic acid (HCN) by reaction in a reflux system of a mineral acid in the presence of cuprous ion.
4. Sample Handling and Preservation
   4.1 The sample should be collected in plastic bottles of 1 liter or larger size. All bottles must be thoroughly cleansed and thoroughly rinsed to remove soluble material from containers.
   4.2 Samples must be preserved with 2 ml of 10 N sodium hydroxide per liter of sample ($pH \geq 12$) at the time of collection.

4.3 Samples should be analyzed as rapidly as possible after collection. If storage is required, the samples should be stored in a refrigerator or in an ice chest filled with water and ice to maintain temperature at 4°C.

4.4 Oxidizing agents such as chlorine decompose most of the cyanides. Test a drop of the sample with potassium iodide-starch test paper (KI-starch paper); a blue color indicates the need for treatment. Add ascorbic acid, a few crystals at a time, until a drop of sample produces no color on the indicator paper. Then add an additional 0.6 g of ascorbic acid for each liter of sample volume.

5. Interferences

5.1 Interferences are eliminated or reduced by using the distillation procedure described in Procedure (8.1 through 8.5).

5.2 Sulfides adversely affect the colorimetric and titration procedures. If a drop of the sample on lead acetate test paper indicates the presence of sulfides, treat 25 ml more of the stabilized sample ($pH \geq 12$) than that required for the cyanide determination with powdered cadmium carbonate. Yellow cadmium sulfide precipitates if the sample contains sulfide. Repeat this operation until a drop of the treated sample solution does not darken the lead acetate test paper. Filter the solution through a dry filter paper into a dry beaker, and from the filtrate, measure the sample to be used for analysis. Avoid a large excess of cadmium and a long contact time in order to minimize a loss by complexation or occlusion of cyanide on the precipitated material.

5.3 Fatty acids will distill and form soaps under the alkaline titration conditions, making the end point almost impossible to detect.

5.3.1 Acidify the sample with acetic acid (1+9) to pH 6.0 to 7.0.

Caution: This operation must be performed in the hood and the sample left there until it can be made alkaline again after the extraction has been performed.

5.3.2 Extract with iso-octane, hexane, or chloroform (preference in order named) with a solvent volume equal to 20% of the sample volume. One extraction is usually adequate to reduce the fatty acids below the interference level. Avoid multiple extractions or a long contact time at low pH in order to keep the loss of HCN at a minimum. When the extraction is completed, immediately raise the pH of the sample to above 12 with NaOH solution.

6. Apparatus

6.1 Reflux distillation apparatus such as shown in Figure 1 or Figure 2. The boiling flask should be of 1 liter size with inlet tube and provision for condenser. The gas absorber may be a Fisher-Milligan scrubber.

6.2 Microburet, 5.0 ml (for titration).

6.3 Spectrophotometer suitable for measurements at 578 nm or 620 nm with a 1.0 cm cell or larger.

7. Reagents

7.1 Sodium hydroxide solution: Dissolve 50 g of NaOH in distilled water, and dilute to 1 liter with distilled water.

7.2 Cadmium carbonate: powdered.

7.3 Ascorbic acid: crystals.

7.4 Cuprous Chloride Reagent: Weigh 20 g of finely powdered Cu_2Cl_2 into an 800 ml beaker. Wash twice, by decantation, with 250 ml portions of dilute sulfuric acid (H_2SO_4, 1 + 49) and then twice with water. Add about 250 ml of water and then hydrochloric acid (HCl, sp gr 1.19) "cautiously" until the salt dissolves (See Note 1). Dilute to 1 liter with distilled water and store in a tightly stoppered bottle containing a few lengths of pure copper wire or rod extending from the bottom to the mouth of the bottle (See Note 2).

Note 1: Approximately 100 ml of HCl will be required for dissolution. The reagent should be clear; dark discoloration indicates the presence of cupric salts.

Note 2: If it is desired to use a reagent bottle of smaller volume, it should be kept completely filled and tightly stoppered. Refill it from the stock solution after each use.

7.5 Sulfuric acid: concentrated.

7.6 Sodium dihydrogenphosphate, 1 M: Dissolve 138 g of $NaH_2PO_4 \cdot H_2O$ in 1 liter of distilled water. Refrigerate this solution.

7.7 Stock cyanide solution: Dissolve 2.51 g of KCN and 2 g KOH in 1 liter of distilled water. Standardize with 0.0192 N $AgNO_3$. Dilute to appropriate concentration so that 1 ml = 1 mg CN.

7.8 Standard cyanide solution, intermediate: Dilute 10.0 ml of stock (1 ml = 1 mg CN) to 1000 ml with distilled water (1 ml = 10μg).

7.9 Standard cyanide solution: Prepare fresh daily by diluting 100.0 ml of intermediate cyanide solution to 1000 ml with distilled water and store in a glass stoppered bottle. 1 ml = 1.0μg CN (1.0 mg/1).

7.10 Standard silver nitrate solution, 0.0192 N: Prepare by crushing approximately 5 g $AgNO_3$ crystals and drying to constant weight at 40°C. Weigh out 3.2647 g of dried $AgNO_3$, dissolve in distilled water, and dilute to 1000 ml (1 ml = mg CN).

7.11 Rhodanine indicator: Dissolve 20 mg of p-dimethyl-amino-benzalrhodanine in 100 ml of acetone.

7.12 Chloramine T solution: Dissolve 1.0 g of white, water soluble Chloramine T in 100 ml of distilled water and refrigerate until ready to use. Prepare fresh weekly.

7.13 Color Reagent – One of the following may be used:

7.13.1 Pyridine-Barbituric Acid Reagent: Place 15 g of barbituric acid in a 250 ml volumetric flask and add just enough distilled water to wash the sides of the flask and wet the barbituric acid. Add 75 ml of pyridine and mix. Add 15 ml of HCl (sp gr 1.19), mix, and cool to room temperature. Dilute to 250 ml with distilled water and mix. This reagent is stable for approximately six months if stored in a cool, dark plate.

7.13.2 Pyridine-pyrazolone solution:

7.13.2.1 3-Methyl-1-phenyl-2-pyrazolin-5-one reagent, saturated solution. Add 0.25 g of 3-methyl-1-phenyl-2-pyrazolin-5-one to 50 ml of distilled water, heat to 60°C with stirring. Cool to room temperature.

7.13.2.2 3,3'Dimethyl-1,1'-diphenyl-[4,4'-bi-2 pyrazoline]-5,5'dione (bispyrazolone). Dissolve 0.01 g of bispyrazolone in 10 ml of pyridine.

7.13.2.3 Pour solution (7.13.2.1) through nonacid-washed filter paper. Collect the filtrate. Through the same filter paper pour solution (7.13.2.2) collecting the filtrate in the same container as filtrate from (7.13.2.1). Mix until the filtrates are homogeneous. The mixed reagent develops a pink color but this does not affect the color production with cyanide if used within 24 hours of preparation.

8. Procedure

8.1 Place 500 ml of sample, or an aliquot diluted to 500 ml in the 1 liter boiling flask. Add 50 ml of sodium hydroxide (7.1) to the absorbing tube and dilute if necessary with distilled water to obtain an adequate depth of liquid in the absorber. Connect the boiling flask, condenser, absorber and trap in the train.

8.2 Start a slow stream of air entering the boiling flask by adjusting the vacuum source. Adjust the vacuum so that approximately one bubble of air per second enters the boiling flask through the air inlet tube.

Caution: The bubble rate will not remain constant after the reagents have been added and while heat is being applied to the flask. It will be necessary to readjust the air rate occasionally to prevent the solution in the boiling flask from backing up into the air inlet tube.

8.3 Slowly add 25 ml conc. sulfuric acid (7.5) through the air inlet tube. Rinse the tube with distilled water and allow the airflow to mix the flask contents for 3 min. Pour 10 ml of Cu_2Cl_2 reagent (7.4) into the air inlet and wash down with a stream of water.

8.4 Heat the solution to boiling, taking care to prevent the solution from backing up into and overflowing from the air inlet tube. Reflux for one hour. Turn off heat and continue the airflow for at least 15 minutes. After cooling the boiling flask, disconnect absorber and close off the vacuum source.

8.5 Drain the solution from the absorber into a 250 ml volumetric flask and bring up to volume with distilled water washings from the absorber tube.

8.6 Withdraw 50 ml of the solution from the volumetric flask and transfer to a 100 ml volumetric flask. Add 15 ml of sodium phosphate solution (7.6) and 2.0 ml of Chloramine T solution (7.12) and mix. Immediately add 5.0 ml pyridine-barbituric acid solution (7.13.1), or pyridine-pyrazolone solution (7.13.2.3), mix and bring to mark with distilled water and mix again.

NOTE: If 2 ml chloramine T solution produces a precipitate with pyridine-pyrazolone, use a lesser amount (0.2 ml) making certain that an excess of chlorine is present.

8.7 For pyridine-pyrazolone solution allow 40 minutes for color development then read absorbance at 620 nm in a 1 cm cell. When using pyridine-barbituric acid, allow 8 minutes for color development then read absorbance at 578 nm in a 1.0 cm cell within 15 minutes.

8.8 Prepare a series of standards by diluting suitable volumes of standard solution to 500.0 ml with distilled water as follows:

ml of Standard Solution (1.0 = 1μg CN)	Conc., When Diluted to 500 ml, mg/1 CN
0 (Blank)	0
5.0	0.01
10.0	0.02
20.0	0.04
50.0	0.10
100.0	0.20
150.0	0.30
200.0	0.40

8.8.1 Standards must be treated in the same manner as the samples, as outlined in (8.1) through (8.7) above.

8.8.2 Prepare a standard curve by plotting absorbance of standard vs. cyanide concentrations.

8.8.3 Subsequently, at least two standards (a high and a low) should be treated as in (8.8.1) to verify standard curve. If results are not comparable (±20%), a complete new standard curve must be prepared.

8.8.4 To check the efficiency of the sample distillation, add an increment of cyanide from either the intermediate standard (7.8) or the working standard (7.9) to insure a level of 20μg/1 or a significant increase in absorbance value. Proceed with the analysis as in Procedure (8.8.1) using the same flask and system from which the previous sample was just distilled.

8.9 Alternatively, if the sample contains more than 1 mg of CN transfer the distillate, or a suitable aliquot diluted to 250 ml, to a 500 ml Erlenmeyer flask. Add 10-12 drops of the benzalrhodanine indicator.

8.10 Titrate with standard silver nitrate to the first change in color from yellow to brownish-pink. Titrate a distilled water blank using the same amount of sodium hydroxide and indicator as in the sample.

8.11 The analyst should familiarize himself with the end point of the titration and the amount of indicator to be used before actually titrating the samples. A 5 or 10 ml microburet may be conveniently used to obtain a more precise titration.

9. Calculation

9.1 Using the colorimetric procedure, calculate concentration of CN, mg/l, directly from prepared standard curve compensating for sample dilution if less than 500 ml was used for distillation.

9.2 Using the titrimetric procedure, calculate concentration of CN as follows:

$$\text{CN, mg/l} = \frac{(\text{A-B})\ 1000}{\text{ml original sample}} \times \frac{250}{\text{ml of aliquot titrated}}$$

where:

A = volume of $AgNO_3$ for titration of sample.

B = volume of $AgNO_3$ for titration of blank.

10. Precision and Accuracy

10.1 In a single laboratory (MDQARL), using mixed industrial and domestic waste samples at concentrations of 0.06, 0.13, 0.28 and 0.62 mg/l CN, the standard deviations were ±0.005, ±0.007, ±0.031, and ±0.094, respectively.

10.2 In a single laboratory (MDQARL), using mixed industrial and domestic waste samples at concentrations of 0.28 and 0.62 mg/l CN, recoveries were 85% and 102%, respectively.

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2. Elly, C. T. "Recovery of Cyanides by Modified Serfass Distillation". *Journal Water Pollution Control Federation,* 40:848-856 (1968).
3. ASTM Standards, Part 23, Water: Atmospheric Analysis, p 498, Method D2036-72 Referee Method A (1973).

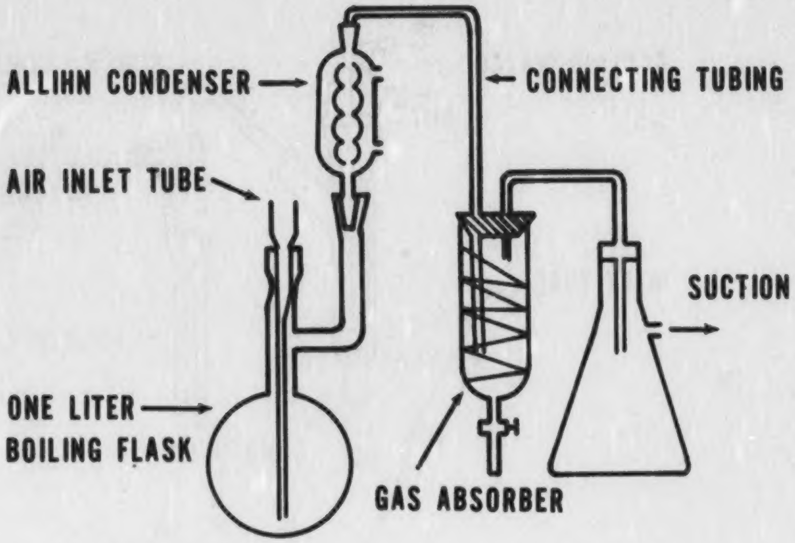
ALLIHN CONDENSER
CONNECTING TUBING
AIR INLET TUBE
SUCTION
ONE LITER BOILING FLASK
GAS ABSORBER

FIGURE 1

CYANIDE DISTILLATION APPARATUS

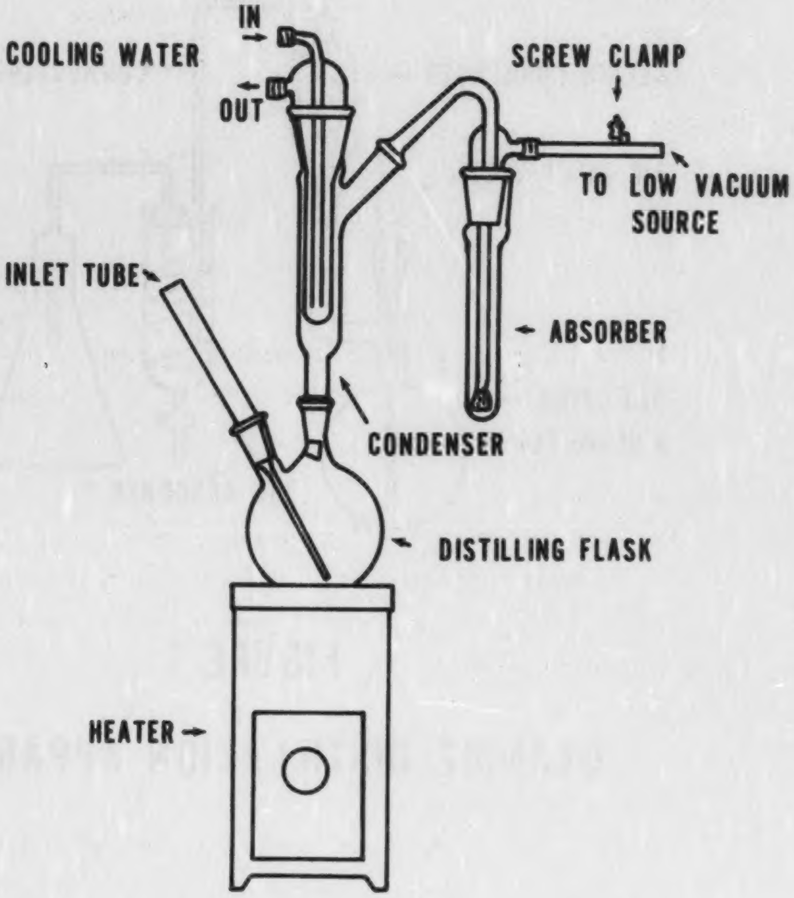
IN
COOLING WATER
OUT
SCREW CLAMP
TO LOW VACUUM SOURCE
INLET TUBE
ABSORBER
CONDENSER
DISTILLING FLASK
HEATER

FIGURE 2
CYANIDE DISTILLATION APPARATUS

CYANIDES, Amenable to Chlorination

STORET NO. 00722

1. Scope and Application

1.1 This method is applicable to the determination of cyanides amenable to chlorination in drinking, surface, and saline waters, and domestic and industrial wastes.

1.2 The titration procedure is used for measuring concentrations of cyanide exceeding 1 mg/1 after removal of the cyanides amenable to chlorination. Below this level the colorimetric determination is used.

2. Summary of Method

2.1 A portion of the sample is chlorinated at a pH>11 to decompose the cyanide. Cyanide levels in the chlorinated sample are then determined by the method for Cyanide, Total, in this manual. Cyanides amenable to chlorination are then calculated by difference.

3. Reagents

3.1 Calcium Hypochlorite solution: Dissolve 5 g of calcium hypochlorite ($Ca(OCl)_2$) in 100 ml of distilled water.

3.2 Sodium Hydroxide solution: Dissolve 50 g of sodium hydroxide (NaOH) in distilled water and dilute to 1 liter.

3.3 Ascorbic acid: crystals.

3.4 Potassium Iodide - starch test paper.

4. Procedure

4.1 Two sample aliquots are required to determine cyanides amenable to chlorination. To one 500 ml aliquot or a volume diluted to 500 ml, add calcium hypochlorite solution (3.1) dropwise while agitating and maintaining the pH between 11 and 12 with sodium hydroxide (3.2).

Caution: The initial reaction product of alkaline chlorination is the very toxic gas cyanogen chloride; therefore, it is recommended that this reaction be performed in a hood. For convenience, the sample may be agitated in a 1 liter beaker by means of a magnetic stirring device.

4.2 Test for residual chlorine with KI-starch paper (3.4) and maintain this excess for one hour, continuing agitation. A distinct blue color on the test paper indicates a sufficient chlorine level. If necessary, add additional hypochlorite solution.

4.3 After one hour, add 0.5 g portions of ascorbic acid (3.3) until KI-starch paper shows no residual chlorine. Add an additional 0.5 g of ascorbic acid to insure the presence of excess reducing agent.

4.4 Test for total cyanide in both the chlorinated and unchlorinated aliquots as in the method Cyanide, Total, in this manual.

5. Calculation

5.1 Calculate the cyanide amenable to chlorination as follows:

CN, mg/1 = A–B

where:

A = mg/1 total cyanide in unchlorinated aliquot

B = mg/1 total in chlorinated aliquot

Bibliography

1. ASTM Standards, Part 23, Water; Atmospheric Analysis, p 503, Method B, D2036-72 (1973).

DISSOLVED OXYGEN

(Modified Winkler With Full-Bottle Technique)

STORET NO. 00300

1. Scope and Application

   1.1 This method is applicable for use with most wastewaters and streams that contain nitrate nitrogen and not more than 1 mg/l of ferrous iron. Other reducing or oxidizing materials should be absent. If 1 ml of fluoride solution is added before acidifying the sample and there is no delay in titration, the method is also applicable in the presence of 100-200 mg/l ferric iron.

   1.2 The Dissolved Oxygen (DO) Probe technique gives comparable results on all sample types.

   1.3 The azide modification is not applicable under the following conditions: (a) samples containing sulfite, thiosulfate, polythionate, appreciable quantities of free chlorine or hypochlorite; (b) samples high in suspended solids; (c) samples containing organic substances which are readily oxidized in a highly alkaline solution. or which are oxidized by free iodine in an acid solution; (d) untreated domestic sewage; (e) biological flocs; and (f) where sample color interferes with endpoint detection. In instances where the azide modification is not applicable, the DO probe should be used.

2. Summary of Method

   2.1 The sample is treated with manganous sulfate, potassium hydroxide, and potassium iodide (the latter two reagents combined in one solution) and finally sulfuric acid. The initial precipitate of manganous hydroxide, $Mn(OH)_2$, combines with the dissolved oxygen in the sample to form a brown precipitate, manganic hydroxide, $MnO(OH)_2$. Upon acidification, the manganic hydroxide forms manganic sulfate which acts as an oxidizing agent to release free iodine from the potassium iodine. The iodine, which is stoichiometrically equivalent to the dissolved oxygen in the sample is then titrated with sodium thiosulfate or phenylarsine oxide (PAO).

3. Interferences

   3.1 There are a number of interferences to the dissolved oxygen test, including oxidizing and reducing agents, nitrate ion, ferrous iron, and organic matter.

   3.2 Various modifications of the original Winkler procedure for dissolved oxygen have been developed to compensate for or eliminate interferences. The Alsterberg modification is commonly used to successfully eliminate the nitrite interference, the Rideal-Stewart modification is designed to eliminate ferrous iron interference, and the Theriault procedure is used to compensate for high concentration of organic materials.

3.3 Most of the common interferences in the Winkler procedure may be overcome by use of the dissolved oxygen probe.

4. Sample Handling and Preservation

4.1 Where possible, collect the sample in a 300 ml BOD incubation bottle. Special precautions are required to avoid entrainment or solution of atmospheric oxygen or loss of dissolved oxygen.

4.2 Where samples are collected from shallow depths (less than 5 feet), use of an APHA-type sampler is recommended. Use of a Kemmerer type sampler is recommended for samples collected from depths of greater than 5 feet.

4.3 When a Kemmerer sampler is used, the BOD sample bottle should be filled to overflowing. (Overflow for approximately 10 seconds). Outlet tube of Kemmerer should be inserted to bottom of BOD bottle. Care must be taken to prevent turbulence and the formation of bubbles when filling bottle.

4.4 At time of sampling, the sample temperature should be recorded as precisely as required.

4.5 Do not delay the determination of dissolved oxygen in samples having an appreciable iodine demand or containing ferrous iron. If samples must be preserved either method (4.5.1) or (4.5.2) below, may be employed.

4.5.1 Add 2 ml of manganous sulfate solution (6.1) and then 2 ml of alkaline iodide-azide solution (6.2) to the sample contained in the BOD bottle. Both reagents must be added well below the surface of the liquid. Stopper the bottle immediately and mix the contents thoroughly. The sample should be stored at the temperature of the collection water, or water sealed and kept at a temperature of 10 to 20°C, in the dark. Complete the procedure by adding 2 ml H_2SO_4 (see 7.1) at time of analysis.

4.5.2 Add 0.7 ml of conc. H_2SO_4 (6.3) and 1 ml sodium azide solution (2 g NaN_3 in 100 ml distilled water) to the sample in the BOD bottle. Store sample as in (4.5.1). Complete the procedure using 2 ml of manganous sulfate solution (6.1), 3 ml alkaline iodide-azide solution (6.2), and 2 ml of conc. H_2SO_4 (6.3) at time of analysis.

4.6 If either preservation technique is employed, complete the analysis within 4-8 hours after sampling.

5. Apparatus

5.1 Sample bottles – 300 ml ±3 ml capacity BOD incubation bottles with tapered ground glass pointed stoppers and flared mouths.

5.2 Pipets – with elongated tips capable of delivering 2.0 ml ±0.10 ml of reagent.

6. Reagents

6.1 Manganous sulfate solution: Dissolve 480 g manganous sulfate ($MnSO_4 \cdot 4H_2O$) in distilled water and dilute to 1 liter.

6.1.1 Alternatively, use 400 g of $MnSO_4 \cdot 2H_2O$ or 364 g of $MnSO_4 \cdot H_2O$ per liter. When uncertainty exists regarding the water of crystallization, a solution of equivalent strength may be obtained by adjusting the specific gravity of the solution to 1.270 at 20°C.

6.2 Alkaline iodide-azide solution: Dissolve 500 g of sodium hydroxide (NaOH) or 700 g of potassium hydroxide (KOH) and 135 g of sodium iodide (NaI) or 150 g of potassium iodide (KI) in distilled water and dilute to 1 liter. To this solution add 10 g of sodium azide (NaN_3) dissolved in 40 ml of distilled water.

6.3 Sulfuric acid: concentrated.

6.4 Starch solution: Prepare an emulsion of 10 g soluble starch in a mortar or beaker with a small quantity of distilled water. Pour this emulsion into 1 liter of boiling water, allow to boil a few minutes, and let settle overnight. Use the clear supernate. This solution may be preserved by the addition of 5 ml per liter of chloroform and storage in a 10°C refrigerator.

6.4.1 Dry, powdered starch indicators such as "thyodene" may be used in place of starch solution.

6.5 Potassium fluoride solution: Dissolve 40 g $KF \cdot 2H_2O$ in distilled water and dilute to 100 ml.

6.6 Sodium thiosulfate, stock solution, 0.75 N: Dissolve 186.15 g $Na_2S_2O_3 \cdot 5H_2O$ in boiled and cooled distilled water and dilute to 1 liter. Preserve by adding 5 ml chloroform.

6.7 Sodium thiosulfate standard titrant, 0.0375 N: Prepare by diluting 50.0 ml of stock solution to 1 liter. Preserve by adding 5 ml of chloroform. Standard sodium thiosulfate, exactly 0.0375 N is equivalent to 0.300 mg of DO per 1.00 ml. Standardize with 0.0375 N potassium biiodate.

6.8 Potassium biiodate standard, 0.0375 N: For stock solution, dissolve 4.873 g of potassium biiodate, previously dried 2 hours at 103°C, in 1000 ml of distilled water. To prepare working standard, dilute 250 ml to 1000 ml for 0.0375 N biiodate solution.

6.9 Standardization of 0.0375 N sodium thiosulfate: Dissolve approximately 2 g (±1.0 g) KI in 100 to 150 ml distilled water; add 10 ml of 10% H_2SO_4 followed by 20.0 ml standard potassium biiodate (6.8). Place in dark for 5 minutes, dilute to 300 ml, and titrate with the standard sodium thiosulfate (6.7) to a pale straw color. Add 1-2 ml starch solution and continue the titration drop by drop until the blue color disappears. Run in duplicate. Duplicate determinations should agree within ±0.05 ml.

6.10 As an alternative to the sodium thiosulfate, phenylarsine oxide (PAO) may be used. This is available, already standardized, from commercial sources.

7. Procedure

7.1 To the sample collected in the BOD incubation bottle, add 2 ml of the manganous sulfate solution (6.1) followed by 2 ml of the alkaline iodide-azide solution (6.2), well below the surface of the liquid; stopper with care to exclude air bubbles, and mix well by inverting the bottle several times. When the precipitate settles, leaving a clear supernatant above the manganese hydroxide floc, shake again. When settling has produced at least 200 ml of clear supernant, carefully remove the stopper and immediately add 2 ml of conc. H_2SO_4 (6.3)(sulfamic acid packets, 3 g may be substituted for H_2SO_4)(1) by allowing the acid to run down the neck of the bottle, re-stopper, and mix by gentle inversion until the iodine is uniformly distributed throughout the bottle. Complete the analysis within 45 minutes.

7.2 Transfer the entire bottle contents by inversion into a 500 ml wide mouth flask and titrate with 0.0375 N thiosulfate solution (6.7) (0.0375 N phenyarsine oxide (PAO) may be substituted as titrant) to a pale straw color. Add 1-2 ml of starch solution (6.4) or 0.1 g of powdered indicator and continue to titrate to the first disappearance of the blue color.

7.3 If ferric iron is present (100 to 200 ppm), add 1.0 ml of KF (6.5) solution before acidification.

7.4 Occasionally, a dark brown or black precipitate persists in the bottle after acidication. This precipitate will dissolve if the solution is kept for a few minutes longer than usual or, if particularly persistent, a few more drops of H_2SO_4 will effect dissolution.

8. Calculation

8.1 Each ml of 0.0375 sodium thiosulfate (or PAO) titrant is equivalent to 1 mg DO when the entire bottle contents are titrated.

8.2 If the results are desired in milliliters of oxygen gas per liter at 0°C and 760 mm pressure, multiply mg/1 DO by 0.698.

8.3 To express the results as percent saturation at 760 mm atmospheric pressure, the solubility data in Table 218 (Whipple & Whipple Table, p 480, Standard Methods, 13th Edition) may be used. Equations for correcting the solubilities to barometric pressures other than mean sea level are given below the table.

8.4 The solubility of DO in distilled water at any barometric pressure, p (mm Hg), temperature, T°C, and saturated vapor pressure, μ (mm Hg), for the given T, may be calculated between the temperature of 0° and 30°C by:

$$\text{ml/l DO} = \frac{(P-\mu) \times 0.678}{35 + T}$$

and between 30° and 50°C by:

$$\text{ml/l DO} = \frac{(P-\mu) \times 0.827}{49 + T}$$

9. Precision and Accuracy

9.1 Exact data are unavailable on the precision and accuracy of this technique; however, reproducibility is approximately 0.2 ppm of DO at the 7.5 ppm level due to equipment tolerances and uncompensated displacement errors.

Bibliography

1. Kroner, R. C., Longbottom, J. E., Gorman, R. A., "A Comparison of Various Reagents Proposed for Use in the Winkler Procedure for Dissolved Oxygen". PHS Water Pollution Surveillance System Applications and Development, Report #12, Water Quality Section, Basic Data Branch, July 1964.

DISSOLVED OXYGEN
(Electrode)

STORET NO. 00299

1. Scope and Application

    1.1 The probe method for dissolved oxygen is recommended for those samples containing materials which interfere with the modified Winkler procedure such as sulfite, thiosulfate, polythionate, mercaptans, free chlorine or hypochlorite, organic substances readily hydrolyzed in alkaline solutions, free iodine, intense color or turbidity, biological flocs, etc.

    1.2 The probe method is recommended as a substitute for the modified Winkler procedure in monitoring of streams, lakes, outfalls, etc., where it is desired to obtain a continuous record of the dissolved oxygen content of the water under observation.

    1.3 The probe method may be used as a substitute for the modified Winkler procedure in BOD determinations where it is desired to perform nondestructive DO measurements on a sample.

    1.4 The probe method may be used under any circumstances as a substitute for the modified Winkler procedure provided that the probe itself is standardized against the Winkler method on samples free of interfering materials.

    1.5 The electronic readout meter for the output from dissolved oxygen probes is normally calibrated in convenient scale (0 to 10, 0 to 15, 0 to 20 mg/1 for example) with a sensitivity of approximately 0.05 mg/liter.

2. Summary of Method

    2.1 The most common instrumental probes for determination of dissolved oxygen in water are dependent upon electrochemical reactions. Under steady-state conditions, the current or potential can be correlated with DO concentrations. Interfacial dynamics at the probe-sample interface are a factor in probe response and a significant degree of interfacial turbulence is necessary. For precision performance, turbulence should be constant.

3. Sample Handling and Preservation

    3.1 See 4.1, 4.2, 4.3, 4.4 under Modified Winkler Method.

4. Interferences

    4.1 Dissolved organic materials are not known to interfere in the output from dissolved oxygen probes.

4.2 Dissolved inorganic salts are a factor in the performance of dissolved oxygen probe.

4.2.1 Probes with membranes respond to partial pressure of oxygen which in turn is a function of dissolved inorganic salts. Conversion factors for seawater and brackish waters may be calculated from dissolved oxygen saturation versus salinity data. Conversion factors for specific inorganic salts may be developed experimentally. Broad variations in the kinds and concentrations of salts in samples can make the use of a membrane probe difficult.

4.2.2 The thallium probe requires the presence of salts in concentrations which provide a minimum conductivity of approximately 200 micromhos.

4.3 Reactive compounds can interfere with the output or the performance of dissolved oxygen probes.

4.3.1 Reactive gases which pass through the membrane probes may interfere. For example, chlorine will depolarize the cathode and cause a high probe-output. Long-term exposures to chlorine will coat the anode with the chloride of the anode metal and eventually desensitize the probe. Alkaline samples in which free chlorine does not exist will not interfere. Hydrogen sulfide will interfere with membrane probes if the applied potential is greater than the half-wave potential of the sulfide ion. If the applied potential is less than the half-wave potential, an interfering reaction will not occur, but coating of the anode with the sulfide of the anode metal can take place.

4.3.2 Sulfur compounds (hydrogen sulfide, sulfur dioxide and mercaptans, for example) cause interfering outputs from the thallium probe. Halogens do not interfere with the thallium probe.

4.4 At low dissolved oxygen concentrations, pH variation below pH 5 and above pH 9 interfere with the performance of the thallium probe (approximately ±0.05 mg/1 DO per pH unit). The performance of membranes is not affected by pH changes.

4.5 Dissolved oxygen probes are temperature sensitive, and temperature compensation is normally provided by the manufacturer. The thallium probe has a temperature coefficient of 1.0 mv/°C. Membrane probes have a temperature coefficient of 4 to 6 percent/°C dependent upon the membrane employed.

5. Apparatus

5,1 No specific probe or accessory is especially recommended as superior. However, probes which have been evaluated or are in use and found to be reliable are the

Weston & Stack DO Analyzer Model 30, the Yellow Springs Instrument (YSI) Model 54, and the Beckman Fieldlab Oxygen Analyzer.

6. Calibration

   Follow manufacturer instructions.

7. Procedure

   Follow manufacturer instructions.

8. Calculation

   Follow manufacturer instructions.

9. Precision and Accuracy

   Manufacturer's specification claim 0.1 mg/l repeatability with ±1% accuracy.

FLUORIDE, Total
(SPADNS Method with Bellack Distillation)

STORET NO. Total 00951
Dissolved 00950

1. Scope and Application
   - 1.1 This method is applicable to the measurement of fluoride in drinking, surface, and saline waters, domestic and industrial wastes.
   - 1.2 The method covers the range from 0.1 to about 2.5 mg/1 F.
2. Summary of Method
   - 2.1 Following distillation to remove interferences, the sample is treated with the SPADNS reagent. The loss of color resulting from the reaction of fluoride with the zirconyl-SPADNS dye is a function of the fluoride concentration.
3. Comments
   - 3.1 The SPADNS reagent is more tolerant of interfering materials than other accepted fluoride reagents. Reference to Table 121(1), p 169, Standard Methods for the Examination of Waters and Wastewaters, 13th Edition, will help the analyst decide if distillation is required. The addition of the highly colored SPADNS reagent must be done with utmost accuracy because the fluoride concentration is measured as a difference of absorbance in the blank and the sample. A small error in reagent addition is the most prominent source of error in this test.
   - 3.2 Care must be taken to avoid overheating the flask above the level of the solution. This is done by maintaining an even flame entirely under the boiling flask.
4. Precision and Accuracy
   - 4.1 On a sample containing 0.83 mg/1 F with no interferences, 53 analysts using the Bellack distillation and the SPADNS reagent obtained a mean of 0.81 mg/1 F with a standard deviation of ±0.089 mg/1.
   - 4.2 On a sample containing 0.57 mg/1 F (with 200 mg/1 SO_4 and 10 mg/1 Al as interferences) 53 analysts using the Bellack distillation obtained a mean of 0.60 mg F/1 with a standard deviation of ±0.103 mg/1.
   - 4.3 On a sample containing 0.68 mg/1 F (with 200 mg/1 SO_4 2 mg/1 Al and 2.5 mg/1 $[Na(PO_3)_6]$ as interferences), 53 analysts using the Bellack distillation obtained a mean of 0.72 mg/1 F with a standard deviation of ±0.092 mg/1.

     (Analytical Reference Service, Sample 111-B water, Fluoride, August, 1961.)

5. Reference

5.1 The procedure to be used for this determination is found in:

Standard Methods for the Examination of Water and Wastewaters, p 171-172 (Method No. 121A, Preliminary Distillation Step) and p 174-176 (Method 121 C, SPADNS) 13th Edition, (1971).

ASTM Standards, Part 23, Water; Atmospheric Analysis, p 312, Method D 1179-72, (1973).

FLUORIDE

(Automated Complexone Method)

STORET NO. 00950

1. Scope and Application
   1.1 This method is applicable to drinking, surface, and saline waters, domestic and industrial wastes. The applicable range of the method is 0.05 to 1.5 mg F/1. Twelve samples per hour can be analyzed.
   1.2 For Total or Total Dissolved Fluoride, the Bellack Distillation must be performed on the samples prior to analysis by the complexone method.
2. Summary of Method
   2.1 Fluoride ion reacts with the red cerous chelate of alizarin complexone. It is unlike other fluoride procedures in that a positive color is developed as contrasted to a bleaching action in previous methods.
3. Sample Handling and Preservation
   3.1 No special requirements.
4. Interferences
   4.1 Method is free from most anionic and cationic interferences, except aluminum, which forms an extremely stable fluoro compound, AlF_6^{-3}. This is overcome by treatment with 8-hydroxyquinoline to complex the aluminum and by subsequent extraction with chloroform. At aluminum levels below 0.2 mg/1, the extraction procedure is not required.

5. Apparatus
   5.1 Technicon AutoAnalyzer Unit consisting of:
      5.1.1 Sampler I.
      5.1.2 Manifold.
      5.1.3 Proportioning pump.
      5.1.4 Continuous filter.
      5.1.5 Colorimeter equipped with 15 mm tubular flow cell and 650 nm filters.
      5.1.6 Recorder equipped with range expander.
6. Reagents
   6.1 Sodium acetate solution: Dissolve 272 g (2 moles) of sodium acetate in distilled water and dilute to 1 liter.
   6.2 Acetic acid-8-hydroxyquinoline solution: Dissolve 6 g of 8-hydroxyquinoline in 34 ml of conc. acetic acid, and dilute to 1 liter with distilled water.

6.3 Chloroform: Analytical reagent grade.

6.4 Ammonium acetate solution (6.7%): Dissolve 67 g of ammonium acetate in distilled water and dilute to 1 liter.

6.5 Hydrochloric acid (2 N): Dilute 172 ml of conc. HCl to 1 liter.

6.6 Lanthanum alizarin fluoride blue solution(1): Dissolve 0.18 g of alizarin fluoride blue in a solution containing 0.5 ml of conc. ammonium hydroxide and 15 ml of 6.7% ammonium acetate (6.4). Add a solution that contains 41 g of anhydrous sodium carbonate and 70 ml of glacial acetic acid in 300 ml of distilled water. Add 250 ml of acetone. Dissolve 0.2 g of lanthanum oxide in 12.5 ml of 2 N hydrochloric acid (6.5) and mix with above solution. Dilute to 1 liter.

6.7 Stock solution: Dissolve 2.210 g of sodium fluoride in 100 ml of distilled water and dilute to 1 liter in a volumetric flask. 1.0 ml = 1.0 mg F.

6.8 Standard Solution: Dilute 10.0 ml of stock solution to 1 liter in a volumetric flask. 1.0 ml = 0.01 mg F.

6.8.1 Using standard solution, prepare the following standards in 100 ml volumetric flasks:

mg F/l	ml Standard Solution/100 ml
0.05	0.5
0.10	1.0
0.20	2.0
0.40	4.0
0.60	6.0
0.80	8.0
1.00	10.0
1.20	12.0
1.50	15.0

7. Procedure

7.1 Set up manifold as shown in Figure 1.

7.2 Allow both colorimeter and recorder to warm up for 30 minutes. Run a baseline with all reagents, feeding distilled water through the sample line. Adjust dark current and operative opening on colorimeter to obtain stable baseline.

7.3 Place distilled water wash tubes in alternate openings in Sampler and set sample timing at 2.5 minutes.

7.4 Arrange fluoride standards in Sampler in order of decreasing concentration. Complete loading of Sampler tray with unknown samples.

7.5 Switch sample line from distilled water to Sampler and begin analysis.

8. Calculation

8.1 Prepare standard curve by plotting peak heights of processed fluoride standards against concentration values. Compute concentration of samples by comparing sample peak heights with standard curve.

9. Precision and Accuracy

9.1 In a single laboratory (MDQARL), using surface water samples at concentrations of 0.06, 0.15, and 1.08 mg F/l, the standard deviation was ±0.018.

9.2 In a single laboratory (MDQARL), using surface water samples at concentrations of 0.14 and 1.25 mg F/l, recoveries were 89% and 102%, respectively.

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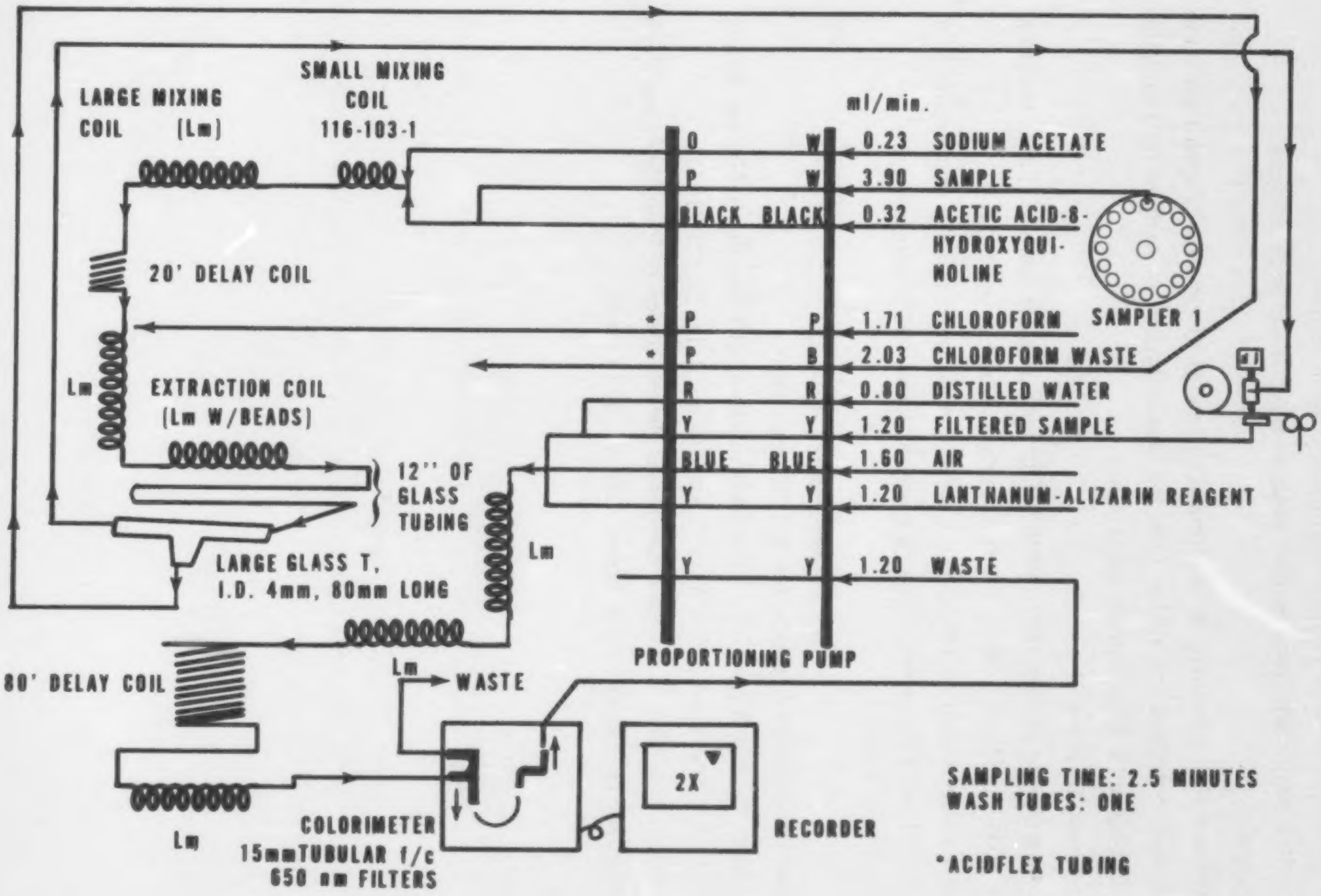
1. J. T. Baker Laboratory Chemical No. J112 or equivalent.
2. Greenhaigh, R., and Riley, J. P., "The Determination of Fluorides in Natural Waters, with Particular Reference to Sea Water". Anal. Chim. Acta, 25, 179 (1961).
3. Chan, K. M., and Riley, J. P., "The Automatic Determination of Fluoride in Sea Water and Other Natural Waters". Anal. Chim. Acta, *35,* 365 (1966).


LARGE MIXING COIL (Lm)
SMALL MIXING COIL 116-103-1
ml/min.
O W 0.23 SODIUM ACETATE
P W 3.90 SAMPLE
BLACK BLACK 0.32 ACETIC ACID-8-HYDROXYQUINOLINE
20' DELAY COIL
* P P 1.71 CHLOROFORM
SAMPLER 1
* P B 2.03 CHLOROFORM WASTE
R R 0.80 DISTILLED WATER
Lm
EXTRACTION COIL (Lm W/BEADS)
Y Y 1.20 FILTERED SAMPLE
BLUE BLUE 1.60 AIR
12'' OF GLASS TUBING
Y Y 1.20 LANTHANUM-ALIZARIN REAGENT
Lm
LARGE GLASS T, I.D. 4mm, 80mm LONG
Y Y 1.20 WASTE
PROPORTIONING PUMP
80' DELAY COIL
Lm
WASTE
2X
COLORIMETER 15mmTUBULAR f/c 650 nm FILTERS
RECORDER
Lm

SAMPLING TIME: 2.5 MINUTES
WASH TUBES: ONE

*ACIDFLEX TUBING

FIGURE 1. FLUORIDE MANIFOLD AA-I

FLUORIDE

(Electrode)

STORET NO: Total 00951
Dissolved 00950

1. Scope and Application
   - 1.1 This method is applicable to the measurement of fluoride in drinking, surface, and saline waters, domestic and industrial wastes.
   - 1.2 Concentration of fluoride from 0.1 up to 1000 mg/liter may be measured.
   - 1.3 For Total or Total Dissolved Fluoride, the Bellack distillation must be performed on the samples prior to electrode analysis.
2. Summary of Method
   - 2.1 The fluoride is determined potentiometrically using a selective ion fluoride electrode in conjunction with a standard single junction sleeve-type reference electrode and a pH meter having an expanded millivolt scale or a selective ion meter having a direct concentration scale for fluoride.
   - 2.2 The fluoride electrode consists of a lanthanum fluoride crystal across which a potential is developed by fluoride ions. The cell may be represented by Ag/Ag Cl, Cl^- (0.3), F^- (0.001) LaF/test solution/SCE/.
3. Interferences
   - 3.1 Extremes of pH interfere; sample pH should be between 5 and 9. Polyvalent cations of Si^{+4}, Fe^{+3} and Al^{+3} interfere by forming complexes with fluoride. The degree of interference depends upon the concentration of the complexing cations, the concentration of fluoride and the pH of the sample. The addition of a pH 5.0 buffer (described below) containing a strong, chelating agent preferentially complexes aluminum (the most common interference), silicon, and iron and eliminates the pH problem.
4. Sampling Handling and Preservation
   - 4.1 No special requirements.
5. Apparatus
   - 5.1 Electrometer (pH meter), with expanded mv scale, or a selective ion meter such as the Orion 400 Series.
   - 5.2 Fluoride Ion Activity Electrode, such as Orion No. 94-09(1).
   - 5.3 Reference electrode, single junction, sleeve-type, such as Orion No. 90-01, Beckman No. 40454, or Corning No. 476010.
   - 5.4 Magnetic Mixer, Teflon-coated stirring bar.

6. Reagents

6.1 Buffer solution, pH 5.0-5.5: To approximately 500 ml of distilled water in a 1 liter beaker add 57 ml of glacial acetic acid, 58 g of sodium chloride and 2 g of CDTA[2]. Stir to dissolve and cool to room temperature. Adjust pH of solution to between 5.0 and 5.5 with 5 N sodium hydroxide (about 150 ml will be required). Transfer solution to a 1 liter volumetric flask and dilute to the mark with distilled water. For work with brines, additional NaCl should be added to raise the chloride level to twice the highest expected level of chloride in the sample.

6.2 Sodium fluoride, stock solution: 1.0 ml = 0.1 mg F. Dissolve 0.2210 g of sodium fluoride in distilled water and dilute to 1 liter in a volumetric flask. Store in chemical-resistant glass or polyethylene.

6.3 Sodium fluoride, standard solution: 1.0 ml = 0.01 mg F. Dilute 100.0 ml of sodium fluoride stock solution (6.2) to 1000 ml with distilled water.

7. Calibration

7.1 Prepare a series of standards using the fluoride standard solution (6.3) in the range of 0 to 2.00 mg/l by diluting appropriate volumes to 50.0 ml. The following series may be used:

Milimeters of Standard (1.0 ml = 0.01 mg/F)	Concentration when Diluted to 50 ml, mg F/liter
0.00	0.00
1.00	0.20
2.00	0.40
3.00	0.60
4.00	0.80
5.00	1.00
6.00	1.20
8.00	1.60
10.00	2.00

7.2 Calibration of Electrometer: Proceed as described in (8.1). Using semilogarithmic graph paper, plot the concentration of fluoride in mg/liter on the log axis vs. the electrode potential developed in the standard on the linear axis, starting with the lowest concentration at the bottom of the scale. Calibration of a selective ion meter: Follow the directions of the manufacturer for the operation of the instrument.

8. Procedure

8.1 Place 50.0 ml of sample or standard solution and 50.0 ml of buffer (See Note) in a 150 ml beaker. Place on a magnetic stirrer and mix at medium speed. Immerse the electrodes in the solution and observe the meter reading while mixing. The electrodes must remain in the solution for at least three minutes or until the reading has stabilized. At concentrations under 0.5 mg/liter F, it may require as long as five minutes to reach a stable meter reading; higher concentrations stabilize more quickly. If a pH meter is used, record the potential measurement for each unknown sample and convert the potential reading to the fluoride ion concentration of the unknown using the standard curve. If a selective ion meter is used, read the fluoride level in the unknown sample directly in mg/l on the fluoride scale.

NOTE: For industrial waste samples, this amount of buffer may not be adequate. Analyst should check pH first. If highly basic (>11), add 1 N HCl to adjust pH to 8.3.

9. Precision and Accuracy

9.1 A synthetic sample prepared by the Analytical Reference Service, PHS, containing 0.85 mg/l fluoride and no interferences was analyzed by 111 analysts; a mean of 0.84 mg/l with a standard deviation of ±0.03 was obtained.

9.2 On the same study, a synthetic sample containing 0.75 mg/l fluoride, 2.5 mg/l polyphosphate and 300 mg/l alkalinity, was analyzed by the same 111 analysts; a mean of 0.75 mg/l fluoride with a standard deviation of ±0.036 was obtained.

Bibliography

1. Patent No. 3,431,182 (March 4, 1969).
2. CDTA is the abbreviated designation of 1, 2-cyclohexylene dinitrilo tetraacetic acid, (Mathieson, Coleman & Bell, Cat. No. P8661) or cyclohexane diamine tetraacetic acid (Merck-Titriplex IV or Baker Cat. No. G083).
3. Standard Methods for the Examination of Water and Wastewaters, p 171, Method No. 121A, Preliminary Distillation Step (Bellack), 13th Edition, 1971.

HARDNESS, Total

STORET NO. 00900

1. Scope and Application
   - 1.1 This method is applicable to drinking, surface, and saline waters, domestic and industrial wastes.
   - 1.2 The method is suitable for all concentration ranges of hardness; however, in order to avoid large titration volumes, use a sample aliquot containing not more than 25 mg $CaCO_3$.
   - 1.3 Automated titration may be used.
2. Summary of Method
   - 2.1 Calcium and magnesium ions in the sample are sequestered upon the addition of disodium ethylenediamine tetraacetate (Na_2EDTA). The end point of the reaction is detected by means of Calmagite Indicator, which has a red color in the presence of calcium and magnesium and a blue color when the cations are sequestered.
3. Comments
   - 3.1 Excessive amounts of heavy metals can interfere. This is usually overcome by complexing the metals with cyanide.
     - 3.1.1 Routine addition of sodium cyanide solution (*Caution:* deadly poison) to prevent potential metallic interference is recommended.
4. Precision and Accuracy
   - 4.1 Forty-three analysts in nineteen laboratories analyzed six synthetic water samples containing exact increments of calcium and magnesium salts, with the following results:

Increment as Total Hardness mg/liter, $CaCO_3$	Precision as Standard Deviation mg/liter, $CaCO_3$	Accuracy as	
		Bias, %	Bias, mg/liter, $CaCO_3$
31	2.87	-0.87	-0.003
33	2.52	-0.73	-0.24
182	4.87	-0.19	-0.4
194	2.98	-1.04	-2.0
417	9.65	-3.35	-13.0
444	8.73	-3.23	-14.3

(FWPCA Method Study 1, Mineral and Physical Analyses)

4.2 In a single laboratory (MDQARL), using surface water samples at an average concentration of 194 mg $CaCO_3$/l, the standard deviation was ±3.

5. References

5.1 The procedure to be used for this determination is found in:

Standard Methods for the Examination of Water and Wastewater, 13th Edition, p 179, Method 122B (1971).

ASTM Standards, Part 23, Water; Atmospheric Analysis, p 169, Method D1126-67 (1973).

HARDNESS, Total
(Automated)

STORET NO. 00900

1. Scope and Application
   1.1 This automated method is applicable to drinking, surface, and saline waters. The applicable range is 10 to 400 mg/l as $CaCO_3$. Approximately 12 samples per hour can be analyzed.
2. Summary of Method
   2.1 The magnesium EDTA exchanges magnesium on an equivalent basis for any calcium and/or other cations to form a more stable EDTA chelate than magnesium. The free magnesium reacts with calmagite at a pH of 10 to give a red-violet complex. Thus, by measuring only magnesium concentration in the final reaction stream, an accurate measurement of total hardness is possible.
3. Sample Handling and Preservation
   3.1 No special requirements.
4. Interferences
   4.1 No significant interferences.
5. Apparatus
   5.1 Technicon AutoAnalyzer consisting of:
      5.1.1 Sampler I.
      5.1.2 Continuous Filter.
      5.1.3 Manifold.
      5.1.4 Proportioning Pump.
      5.1.5 Colorimeter equipped with 15 mm tubular flow cell and 520 nm filters.
      5.1.6 Recorder equipped with range expander.
6. Reagents
   6.1 Buffer: Dissolve 67.6 g NH_4Cl in 572 ml of NH_4OH and dilute to 1 liter with distilled water.
   6.2 Calmagite Indicator: Dissolve 0.25 g in 500 ml of distilled water by stirring approximately 30 minutes on a magnetic stirrer. Filter.
   6.3 Monomagnesium ethylenediamine-tetraacetate (MgEDTA): Dissolve 0.2 g of MgEDTA in 1 liter of distilled water.
   6.4 Stock Solution: Weigh 1.000 g of calcium carbonate (pre-dried at 105°C) into 500 ml Erlenmeyer flask; add 1:1 HCl until all $CaCO_3$ has dissolved. Add 200 ml

of distilled water and boil for a few minutes. Cool, add a few drops of methyl red indicator, and adjust to the orange color with 3N NH_4OH and dilute to 1000 ml with distilled water. 1.0 ml = 1.0 mg $CaCO_3$.

6.4.1 Dilute each of the following volumes of stock solutions to 250 ml in a volumetric flask for appropriate standards:

Stock Solution, ml	$CaCO_3$, mg/l
2.5	10.0
5.0	20.0
10.0	40.0
15.0	60.0
25.0	100.0
35.0	140.0
50.0	200.0
75.0	300.0
100.0	400.0

7. Procedure

7.1 Set up manifold as shown in Figure 1.

7.2 Allow both colorimeter and recorder to warm up for 30 minutes. Run a baseline with all reagents, feeding distilled water through the sample line. Adjust dark current and operative opening on colorimeter to obtain stable baseline.

7.3 Place distilled water wash tubes in alternate openings in Sampler and set sample timing at 2.5 minutes.

7.4 Arrange working standards in Sampler in order of decreasing concentrations. Complete loading of Sampler tray with unknown samples.

7.5 Switch sample line from distilled water to Sampler and begin analysis.

8. Calculation

8.1 Prepare standard curve by plotting peak heights of processed standards against concentration values. Compute concentration of samples by comparing sample peak heights with standard curve.

9. Precision and Accuracy

9.1 In a single laboratory (MDQARL), using surface water samples at concentrations of 19, 120, 385, and 366 mg/l as $CaCO_3$, the standard deviations were ±1.5, ±1.5, ±4.5, and ±5.0, respectively.

9.2 In a single laboratory (MDQARL), using surface water samples at concentrations of 39 and 296 mg/l as $CaCO_3$, recoveries were 89% and 93%, respectively.

Bibliography

1. Technicon AutoAnalyzer Methodology, Bulletin No. 2, Technicon Controls, Inc., Chauncey, New York (July 1960).
2. Standard Methods for the Examination of Water and Wastewater, 13th Edition, p 179, Method 122B (1971).

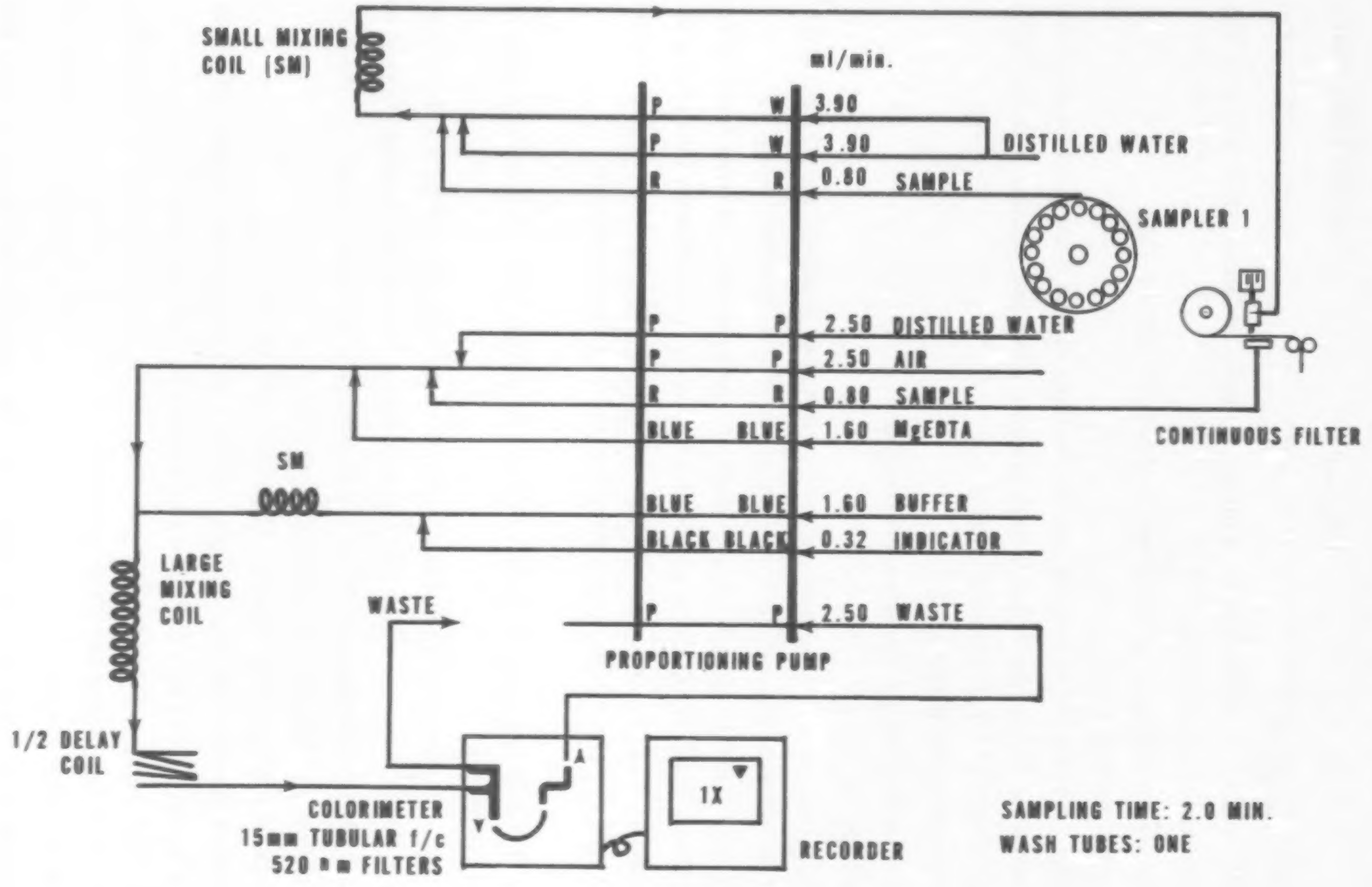

SMALL MIXING COIL (SM)
ml/min.
P
W
3.90
P
W
3.90
DISTILLED WATER
R
R
0.80
SAMPLE
SAMPLER 1
P
P
2.50
DISTILLED WATER
P
P
2.50
AIR
R
R
0.80
SAMPLE
BLUE
BLUE
1.60
MgEDTA
CONTINUOUS FILTER
SM
BLUE
BLUE
1.60
BUFFER
BLACK
BLACK
0.32
INDICATOR
LARGE MIXING COIL
WASTE
P
P
2.50
WASTE
PROPORTIONING PUMP
1/2 DELAY COIL
A
V
COLORIMETER
15mm TUBULAR f/c
520 nm FILTERS
1X
RECORDER
SAMPLING TIME: 2.0 MIN.
WASH TUBES: ONE

FIGURE 1. HARDNESS MANIFOLD AA-I

IODIDE

(Titrimetric)

STORET NO. 71865

1. Scope and Application

   1.1 This method is applicable to drinking, surface, and saline waters, sewage and industrial waste effluents.

   1.2 The concentration range for this method is 2-20 mg/l of iodide.

2. Summary of Method

   2.1 After pretreatment to remove interferences, the sample is analyzed for iodide by converting the iodide to iodate with bromine water and titrating with phenylarsine oxide (PAO) or sodium thiosulfate.

3. Sample Handling and Preservation

   3.1 Store at 4°C and analyze as soon as possible.

4. Interferences

   4.1 Iron, manganese and organic matter can interfere; however, the calcium oxide pretreatment removes or reduces these to insignificant concentrations.

   4.2 Color interferes with the observation of indicator and bromine-water color changes. This interference is eliminated by the use of a pH meter instead of a pH indicator and the use of standardized amounts of bromine water and sodium formate solution instead of observing the light yellow color changes.

5. Reagents

   5.1 Acetic Acid Solution (1:8): Mix 100 ml of glacial acetic acid with 800 ml of distilled water.

   5.2 Bromine Water: In a fume hood, add 0.2 ml bromine to 500 ml distilled water. Stir with a magnetic stirrer and a Teflon-coated stirring bar for several hours or until the bromine dissolves. Store in a glass-stoppered colored bottle.

   5.3 Calcium Oxide (CaO): Anhydrous, powdered.

   5.4 Potassium Iodide (KI): Crystals, ACS Reagent Grade.

   5.5 Sodium Acetate Solution (275 g/l): Dissolve 275 g of sodium acetate trihydrate ($NaC_2H_3O_2 \cdot 3H_2O$) in distilled water. Dilute to 1 liter and filter.

   5.6 Sodium Formate Solution (500 g/l): Dissolve 50 g of sodium formate ($NaCHO_2$) in hot distilled water and dilute to 100 ml.

   5.7 Nitrogen Gas: cylinder.

   5.8 Sulfuric Acid Solution (1:4): Slowly add 200 ml of H_2SO_4 (sp. gr. 1.84) to 800 ml of distilled water.

5.9 Phenylarsine Oxide (0.0375 N): Hach Chemical Co. or equivalent. Standardize with 0.0375 N potassium biiodate (5.15, 5.18).

5.10 Phenylarsine Oxide Working Standard (0.0075 N): Transfer 100 ml of commercially available 0.0375 N phenylarsine oxide (5.9) to a 500 ml volumetric flask and dilute to the mark with distilled water. This solution should be prepared fresh daily.

5.11 Amylose Indicator: Mallinckrodt Chemical Works or equivalent.

5.12 Sodium Thiosulfate, Stock Solution, 0.75 N: Dissolve 186.15 g ($Na_2S_2O_3 \cdot 5H_2O$) in boiled and cooled distilled water and dilute to 1.0 liter. Preserve by adding 5 ml chloroform.

5.13 Sodium Thiosulfate Standard Titrant, 0.0375 N: Prepare by diluting 50.0 ml of stock solution to 1.0 liter. Preserve by adding 5 ml of chloroform. Standardize with 0.0375 N potassium biiodate (5.15, 5.18).

5.14 Sodium Thiosulfate Working Standard (0.0075 N): Transfer 100 ml of sodium thiosulfate standard titrant (5.13) to a 500 ml volumetric flask and dilute to the mark with distilled water. This solution should be prepared fresh daily.

5.15 Potassium Biiodate Standard, 0.0375 N: Dissolve 4.873 g potassium biiodate, previously dried 2 hours at 103°C, in distilled water and dilute to 1.0 liter. Dilute 250 ml to 1.0 liter for 0.0375 N biiodate solution.

5.16 Starch Solution: Prepare an emulsion of 10 g of soluble starch in a mortar or beaker with a small quantity of distilled water. Pour this emulsion into 1 liter of boiling water, allow to boil a few minutes, and let settle overnight. Use the clear supernate. This solution may be preserved by the addition of 5 ml per liter of chloroform and storage in a 10°C refrigerator. Commercially available, powdered starch indicators may be used in place of starch solution.

5.17 Potassium Fluoride ($KF \cdot 2H_2O$): ACS Reagent Grade

5.18 Standardization of 0.0375 N Phenylarsine Oxide and 0.0375 N sodium thiosulfate: Dissolve approximately 2 g (±1.0 g) KI (5.4) in 100 to 150 ml distilled water; add 10 ml H_2SO_4 solution (5.8) followed by 20 ml standard potassium biiodate solution (5.15). Place in dark for 5 minutes, dilute to 300 ml and titrate with phenylarsine oxide (5.9) or sodium thiosulfate standard titrant (5.13) to a pale straw color. Add a small scoop of indicator (5.11). Wait until homogeneous color develops and continue the titration drop by drop until the blue color disappears. Run in duplicate. Duplicate determinations should agree within ±0.05 ml.

6. Procedure

6.1 Pretreatment

6.1.1 Add a visible excess of CaO (5.3) to 400 ml of sample. Stir or shake vigorously for approximately 5 minutes. Filter through a dry, moderately retentive filter paper, discarding the first 75 ml.

6.2 Iodide Determination

6.2.1 Place 100 ml of pretreated sample (6.1) or a fraction thereof diluted to that volume, into a 150 ml beaker. Add a Teflon-coated stirring bar and place on a magnetic stirrer. Insert a pH electrode and adjust the pH to approximately 7 or slightly less by the dropwise addition of H_2SO_4 solution (5.8).

6.2.2 Transfer the sample to a 250 ml wide-mouthed conical flask. Wash beaker with small amounts of distilled water and add washings to the flask.

NOTE: A 250 ml iodine flask would increase accuracy and precision by preventing possible loss of the iodine generated upon addition of potassium iodide and sulfuric acid (6.3.1).

6.2.3 Add 15 ml sodium acetate solution (5.5) and 5 ml acetic acid solution (5.1). Mix well. Add 40 ml bromine water solution (5.2); mix well. Wait 5 minutes.

6.2.4 Add 2 ml sodium formate solution (5.6); mix well. Wait 5 minutes.

6.2.5 Purge the space above the sample with a gentle stream of nitrogen (5.7) for approximately 30 seconds to remove bromine fumes.

6.2.6 If a precipitate forms (iron), add 0.5 g $KF \cdot 2H_2O$ (5.17).

6.2.7 A distilled water blank must be run with each set of samples because of iodide in reagents. If a blank is consistently shown to be zero for a particular "lot" of chemicals it can then be ignored.

6.3 Titration

6.3.1 Dissolve approximately 1 g potassium iodide (5.4) in sample. Add 10 ml of H_2SO_4 solution (5.8) and place in dark for 5 minutes.

6.3.2 Titrate with phenylarsine oxide working standard (5.10) or sodium thiosulfate working standard solution (5.14) adding indicator (5.11 or 5.15) as end point is approached (light straw color). Titrate to colorless solution. Disregard returning blue color.

7. Calculations

$$I^- \text{ (mg/l)} = 21{,}150 \left[\frac{\text{ml} \times N}{V}\right]$$

ml = the number of ml of PAO need to titrate the sample.

N = the normality of the PAO used to titrate the sample.

V = the volume of sample taken (100 ml or a fraction thereof)

21,150 was calculated from the number of equivalents of iodine produced when the potassium iodide was added and from the rearrangement of the equation to produce the value in terms of mg/l.

8. Precision and Accuracy

8.1 In a single laboratory (MDQARL), using a mixed domestic and industrial waste effluent, at concentrations of 1.6, 4.1, 6.6, 11.6 and 21.6 mg/l of iodide, the standard deviations were ±0.23, ±0.17, ±0.10, ±0.06 and ±0.50 mg/1, respectively.

8.2 In a single laboratory (MDQARL), using a mixed domestic and industrial waste effluent at concentrations of 4.1, 6.6, 11.6 and 21.6 mg/l of iodide, recoveries were 80, 97, 97, and 92%, respectively.

Bibliography

1. ASTM Standards, Part 23, Water; Atmospheric Analysis, p 331-333, Method D1246 C (1973).

METALS

(Atomic Absorption Methods)

1. Scope and Application

1.1 Metals in solution may be readily determined by atomic absorption spectroscopy. The method is simple, rapid, and applicable to a large number of metals in drinking, surface, and saline waters, and domestic and industrial wastes. While drinking waters may be analyzed directly, domestic and industrial wastes require processing to solubilize suspended material. Sludges, sediments and other solid type samples may also be analyzed after proper pretreatment.

1.2 Detection limits, sensitivity and optimum ranges of the metals will vary with the various makes and models of satisfactory atomic absorption spectrophotometers. The data shown in Table 1, however, provide some indication of the actual concentration ranges measurable with conventional atomization. In the majority of instances the concentration range shown in the table may be extended much lower with scale expansion and conversely extended upwards by using a less sensitive wavelength or by rotating the burner 90 degrees. Detection limits may also be extended through concentration of the sample, through solvent extraction techniques and/or the use of the so called furnace techniques. The latter includes the heated graphite atomizer, the carbon rod and the tantalum strip accessories. When using furnace techniques, however, the analyst should be cautioned as to possible chemical reactions occurring at elevated temperatures which may result in either suppression or enhancement of the analysis element. Methods of standard addition are mandatory with these furnace techniques to insure valid data.

1.3 Where conventional, atomic absorption techniques do not provide adequate sensitivity, reference is made to colorimetric or specialized procedures. Examples of these specialized techniques would be the gaseous hydride method for arsenic and selenium and the cold vapor technique for mercury.

1.4 Atomic absorption procedures are provided as the methods of choice; however, other instrumental methods have also been shown to be capable of producing precise and accurate analytical data. These instrumental techniques include emission spectroscopy, X-ray fluorescence, spark source mass spectroscopy, and anodic stripping to name but a few. The analyst should be cautioned that these methods are highly specialized techniques requiring a high degree of skill to interpret results and obtain valid data.

TABLE 1
Atomic Absorption Concentration Ranges With Conventional Atomization***

Metal	Detection Limit mg/l	Sensitivity mg/l	Optimum Concentration Range mg/l
Aluminum	0.1	1	5 – 100
Antimony	0.2	0.5	1 – 40
Arsenic*	0.002	–	0.002 – 0.02
Barium	0.03	0.4	1 – 20
Beryllium	0.005	0.025	0.05 – 2
Cadmium	0.002	0.025	0.05 – 2
Calcium	0.003	0.08	0.2 – 20
Chromium	0.02	0.1	0.2 – 10
Cobalt	0.03	0.2	0.5 – 10
Copper	0.01	0.1	0.2 – 10
Iron	0.02	0.12	0.3 – 10
Lead	0.05	0.5	1 – 20
Magnesium	0.0005	0.007	0.02 – 2
Manganese	0.01	0.05	0.1 – 10
Mercury**	0.0002	–	0.0002 – 0.01
Molybdenum	0.1	0.3	0.5 – 20
Nickel	0.02	0.15	0.3 – 10
Potassium	0.005	0.04	0.1 – 2
Selenium*	0.002	–	0.002 – 0.02
Silver	0.01	0.06	0.1 – 4
Sodium	0.002	0.015	0.03 – 1
Thallium	0.1	0.5	1 – 20
Tin	0.8	4	10 – 200
Titanium	0.3	2	5 – 100
Vanadium	0.2	0.8	1 – 100
Zinc	0.005	0.02	0.05 – 2

*Gaseous hydride method.

**Cold vapor technique.

***The concentrations shown above are not contrived values and should be obtainable with conventional aspiration on any satisfactory atomic absorption spectrophotometer.

2. Summary of Method

2.1 Atomic absorption spectroscopy is similar to flame emission photometry in that a sample is atomized and aspirated into a flame. Flame photometry, however, measures the amount of light emitted, whereas, in atomic absorption spectrophotometry a light beam is directed through the flame into a monochromator, and onto a detector that measures the amount of light absorbed. In many instances absorption is more sensitive because it depends upon the presence of free unexcited atoms and generally the ratio of unexited to excited atoms at a given moment is very high. Since the wavelength of the light beam is characteristic of only the metal being determined, the light energy absorbed by the flame is a measure of the concentration of that metal in the sample. This principle is the basis of atomic absorption spectroscopy.

2.2 Although methods have been reported for the analysis of solids by atomic absorption spectroscopy (Spectrochim Acta, *24B* 53, 1969) the technique generally is limited to metals in solution or solubilized through some form of sample processing.

2.2.1 Preliminary treatment of wastewater and/or industrial effluents is usually necessary because of the complexity and variability of the sample matrix. Suspended material must be solubilized through some form of digestion. This may vary because of the metals to be determined but generally will include a wet digestion with nitric acid.

2.2.2 In those instances where complete characterization of a sample is desired, the suspended material must be analyzed separately. This may be accomplished by filtration and acid digestion of the suspended material. Metallic constituents in this acid digest are subsequently determined and the sum of the dissolved plus suspended concentrations will then provide the total concentrations present. The sample should be filtered as soon as possible after collection and the filtrate acidified immediately.

2.2.3 The total sample may also be treated with acid before filtration to measure what may be termed "extractable" concentrations.

3. Definition of Terms

3.1 Sensitivity: The concentration in milligrams of metal per liter that produces an absorption of 1%.

3.2 Detection Limit: The concentration that produces absorption equivalent to twice the magnitude of the fluctuation in the background (zero absorption).

3.3 Dissolved Metals: Those constituents (metals) which will pass through a 0.45 μ membrane filter.

3.4 Suspended Metals: Those constituents (metals) which are retained by a 0.45 μ membrane filter.

3.5 Total Metals: The concentration of metals determined on an unfiltered sample following vigorous digestion (Section 4.1.3), or the sum of the concentrations of metals in both the dissolved and suspended fractions.

3.6 Extractable Metals: The concentration of metals in an unfiltered sample following treatment with hot dilute mineral acid (Section 4.1.4).

4. Sample Handling and Preservation

4.1 For the determination of trace metals, contamination and loss are of prime concern. Dust in the laboratory environment, impurities in reagents and impurities on laboratory apparatus which the sample contacts are all sources of potential contamination. For liquid samples, containers can introduce either positive or negative errors in the measurement of trace metals by (a) contributing contaminants through leaching or surface desorption and (b) by depleting concentrations through adsorption. Thus the collection and treatment of the sample prior to analysis requires particular attention. The sample bottle should be thoroughly washed with detergent and tap water; rinsed with 1:1 nitric acid, tap water, 1:1 hydrochloric acid, tap water and finally deionized distilled water in that order.

NOTE 1: Chromic acid may be useful to remove organic deposits from glassware; however, the analyst should be cautioned that the glassware must be thoroughly rinsed with water to remove the last traces of chromium. This is especially important if chromium is to be included in the analytical scheme. Chromic acid should not be used with plastic bottles.

Before collection of the sample a decision must be made as to the type of data desired, i.e., dissolved, suspended, total or extractable.

4.1.1 For the determination of dissolved constituents the sample must be filtered through a 0.45 μ membrane filter as soon as practical after collection. (Glass or plastic filtering apparatus are recommended to avoid possible contamination.) Use the first 50-100 ml to rinse the filter flask. Discard this portion and collect the required volume of filtrate. Acidify the filtrate with 1:1 redistilled HNO_3 to a pH of 2. Normally, 3 ml of (1:1) acid per liter should be sufficient to preserve the sample (See Note

2). Analyses performed on a sample so treated shall be reported as "dissolved" concentrations.

NOTE 2: It has been suggested (International Biological Program, Symposium on Analytical Methods, Amsterdam, Oct. 1966) that additional acid, as much as 25 ml of conc. HCl/liter, may be required to stabilize certain types of highly buffered samples if they are to be stored for any length of time. Therefore, special precautions should be observed for preservation and storage of unusual samples intended for metal analysis.

4.1.2 For the determination of suspended metals a representative volume of unpreserved sample must be filtered through a 0.45 μ membrane filter. When considerable suspended material is present, as little as 100 ml of a well mixed sample is filtered.

Record the volume filtered and transfer the membrane filter containing the insoluble material to a 250 ml Griffin beaker and add 3 ml conc. redistilled HNO_3. Cover the beaker with a watch glass and heat gently. The warm acid will soon dissolve the membrane. Increase the temperature of the hot plate and digest the material. When the acid has evaporated, cool the beaker and watch glass and add another 3 ml of conc. redistilled HNO_3.

Cover and continue heating until the digestion is complete, generally indicated by a light colored residue. Add distilled 1:1 HCl (2 ml) to the dry residue and again warm the beaker gently to dissolve the material. Wash down the watch glass and beaker walls with deionized distilled water and filter the sample to remove silicates and other insoluble material that could clog the atomizer. Adjust the volume to some predetermined value based on the expected concentrations of metals present. This volume will vary depending on the metal to be determined. The sample is now ready for analysis. Concentrations so determined shall be reported as "suspended".

4.1.3 For the determination of total metals the sample is acidified with 1:1 redistilled HNO_3 to a pH of 2 at the time of collection. The sample is not filtered before processing. Choose a volume of sample appropriate for the expected level of metals. If much suspended material is present, as little as 50-100 ml of well mixed sample will most probably be sufficient. (The sample volume required may also vary proportionally with the number of metals to be determined).

Transfer a representative aliquot of the well mixed sample to a Griffin beaker and add 3 ml of conc. redistilled HNO_3. Place the beaker on a hot plate and evaporate to dryness cautiously, making certain that the sample does not boil. Cool the beaker and add another 3 ml portion of conc. redistilled HNO_3. Cover the beaker with a watch glass and return to the hot plate. Increase the temperature of the hot plate so that a gentle reflux action occurs. Continue heating, adding additional acid as necessary, until the digestion is complete (generally indicated by a light colored residue). Add sufficient distilled 1:1 HCl and again warm the beaker to dissolve the residue. Wash down the beaker walls and watch glass with distilled water and filter the sample to remove silicates and other insoluble material that could clog the atomizer. Adjust the volume to some predetermined value based on the expected metal concentrations. The sample is now ready for analysis. Concentrations so determined shall be reported as "total" (See Note 3). STORET parameter numbers for reporting this type of data have been assigned and are given for each metal.

NOTE 3: Certain metals such as titanium, silver, mercury, and arsenic require modification of the digestion procedure and the individual sheets for these metals should be consulted.

4.1.4 To determine metals soluble in hot, dilute, HCl – HNO_3, acidify the entire sample at the time of collection with conc. redistilled HNO_3, 5 ml/l. At the time of analysis a 100 ml aliquot of well mixed sample is transferred to a beaker or flask. Five ml of distilled HCl (1:1) is added and the sample heated for 15 minutes at 95°C on a steam bath or hot plate. After this treatment the sample is filtered and the volume adjusted to 100 ml. The sample is then ready for analysis.

The data so obtained are significant in terms of "total" metals in the sample, with the reservation that something less than "total" is probably measured. Concentrations of metal found, especially in heavily silted samples, will be substantially higher than data obtained on only the soluble fraction. STORET parameter numbers for the storage of this type data are not available at this time.

5. Interferences

5.1 The most troublesome type of interference in atomic absorption spectrophotometry is usually termed "chemical" and is caused by lack of absorption of atoms bound in molecular combination in the flame. This phenomenon can occur when the flame is not sufficiently hot to dissociate the molecule, as in the case of phosphate interference with magnesium, or because the dissociated atom is immediately oxidized to a compound that will not dissociate further at the temperature of the flame. The addition of lanthanum will overcome the phosphate interference in the magnesium, calcium and barium determinations. Similarly, silica interference in the determination of manganese can be eliminated by the addition of calcium.

5.1.1 Chemical interferences may also be eliminated by separating the metal from the interfering material. While complexing agents are primarily employed to increase the sensitivity of the analysis, they may also be used to eliminate or reduce interferences.

5.2 The presence of high dissolved solids in the sample may result in an interference from non-atomic absorbance such as light scattering. If background correction is not available, a non-absorbing wavelength should be checked. Preferably, high solids type samples should be extracted (See 5.1.1 and 9.2).

5.3 Ionization interferences occur where the flame temperature is sufficiently high to generate the removal of an electron from a neutral atom, giving a positively charged ion. This type of interference can generally be controlled by the addition, to both standard and sample solutions, of a large excess of an easily ionized element.

5.4 Spectral interference can occur when an absorbing wavelength of an element present in the sample but not being determined falls within the width of the absorption line of the element of interest. The results of the determination will then be erroneously high, due to the contribution of the interfering element to the atomic absorption signal. Spectral interference may sometimes be reduced by narrowing the slit width.

6. Apparatus

6.1 Atomic absorption spectrophotometer: Any commercial atomic absorption instrument having an energy source, an atomizer burner system, a monochromator, and a detector is suitable.

6.2 Burner: The burner recommended by the particular instrument manufacturer should be used. For certain elements the nitrous oxide burner is required.

6.3 Separatory flasks: 250 ml, or larger, for extraction with organic solvents.

6.4 Glassware: All glassware, including sample bottles, should be washed with detergent, rinsed with tap water, 1:1 nitric acid, tap water, 1:1 hydrochloric acid, tap water and deionized distilled water in that order. [See Note 1 under (4.1) concerning the use of chromic acid.]

6.5 Borosilicate glass distillation apparatus.

7. Reagents

7.1 Deionized distilled water: Prepare by passing distilled water through a mixed bed of cation and anion exchange resins. Use deionized distilled water for the preparation of all reagents, calibration standards, and as dilution water.

7.2 Nitric acid (conc.): If metal impurities are found to be present, distill reagent grade nitric acid in a borosilicate glass distillation apparatus. Prepare a 1:1 dilution with deionized distilled water.

Caution: Distillation should be performed in hood with protective sash in place.

7.3 Hydrochloric acid (1:1): Prepare a 1:1 solution of reagent grade hydrochloric acid and deionized distilled water. If metal impurities are found to be present, distill this mixture from a borosilicate glass distillation apparatus.

7.4 Stock metal solutions: Prepare as directed in (8.1) and under the individual metal procedures. Commercially available stock standard solutions may also be used.

7.5 Standard metal solutions: Prepare a series of standards of the metal by dilution of the appropriate stock metal solution to cover the concentration range desired.

7.6 Fuel and oxidant: Commercial grade acetylene is generally acceptable. Air may be supplied from a compressed air line, a laboratory compressor, or from a cylinder of compressed air. Reagent grade nitrous oxide is also required for certain determinations.

7.7 Special reagents for the extraction procedure.

7.7.1 Pyrrolidine dithiocarbamic acid (PDCA): Prepare by adding 18 ml of analytical reagent grade pyrrolidine to 500 ml of chloroform in a liter flask. Cool and add 15 ml of carbon disulfide in small portions and with swirling. Dilute to 1 liter with chloroform. The solution can be used for several months if stored in a brown bottle in a refrigerator.

NOTE: An acceptable grade of pyrrolidine may be obtained from the Aldrich Chemical Co., 940 West St. Paul Ave., Milwaukee, Wi. 53233 (414, 273-3850).

7.7.2 Ammonium hydroxide, 2N: Dilute 3 ml conc. NH_4OH to 100 ml with deionized distilled water.

7.7.3 Bromphenol blue indicator.

7.7.4 HCl: Dilute 2 ml redistilled HCl to 40 ml with deionized distilled water.

8. Preparation of Standards and Calibration

8.1 Stock solutions are prepared from high purity metals, oxides or nonhygroscopic reagent grade salts using redistilled nitric or hydrochloric acids. Sulfuric or phosphoric acids should be avoided as they produce an adverse effect on many elements. The stock solutions are prepared at concentrations of 1000 mg of the metal per liter.

8.2 Standard solutions are prepared by diluting the stock metal solutions at the time of analysis. For best results, calibration standards should be prepared fresh each time an analysis is to be made and discarded after use. Prepare a blank and calibration standards in graduated amounts in the appropriate range. The *calibration standards* should be prepared using the same type of acid (HCl, HNO_3 or H_2SO_4) and at the same concentration as will result in the samples following processing. As filtered water samples are preserved with 1:1 redistilled HNO_3 (3 ml per liter), calibration standards for these analyses should be similarly prepared with HNO_3. Samples processed for suspended metals (4.1.2) or total metals (4.1.3) should be analyzed using calibration standards prepared in HCl. Beginning with the blank and working toward the highest standard, aspirate the solutions and record the readings. Repeat the operation with both the calibration standards and the samples a sufficient number of times to secure a reliable average reading for each solution.

8.3 Where the sample matrix is so complex that viscosity, surface tension and components cannot be accurately matched with standards, the method of standard addition must be used. This technique relies on the addition of small, known amounts of the analysis element to portions of the sample – the absorbance difference between those and the original solution giving the slope of the calibration curve. The method of standard addition is described in greater detail in (8.5).

8.4 For those instruments which do not read out directly in concentration, a calibration curve is prepared to cover the appropriate concentration range. Usually, this means the preparation of standards which produce an absorption of 0 to 80 percent. The correct method is to convert the percent absorption readings to absorbance and plot that value against concentration. The following relationship is used to convert absorption values to absorbance:

absorbance = log (100/%T) = 2 – log % T

where % T = 100 – % absorption

As the curves are frequently nonlinear, especially at high absorption values, the number of standards should be increased in that portion of the curve.

8.5 Standard Addition Method: In this method, equal volumes of sample are added to a deionized distilled water blank and to three standards containing different known amounts of the test element. The volume of the blank and the standards must be the same. The absorbance of each solution is determined and then plotted on the vertical axis of a graph, with the concentrations of the known standards plotted on the horizontal axis. When the resulting line is extrapolated back to zero absorbance, the point of interception of the abscissa is the concentration of the unknown. The abscissa on the left of the ordinate is scaled the same as on the right side, but in the opposite direction from the ordinate. An example of a plot so obtained is shown in Fig. 1.

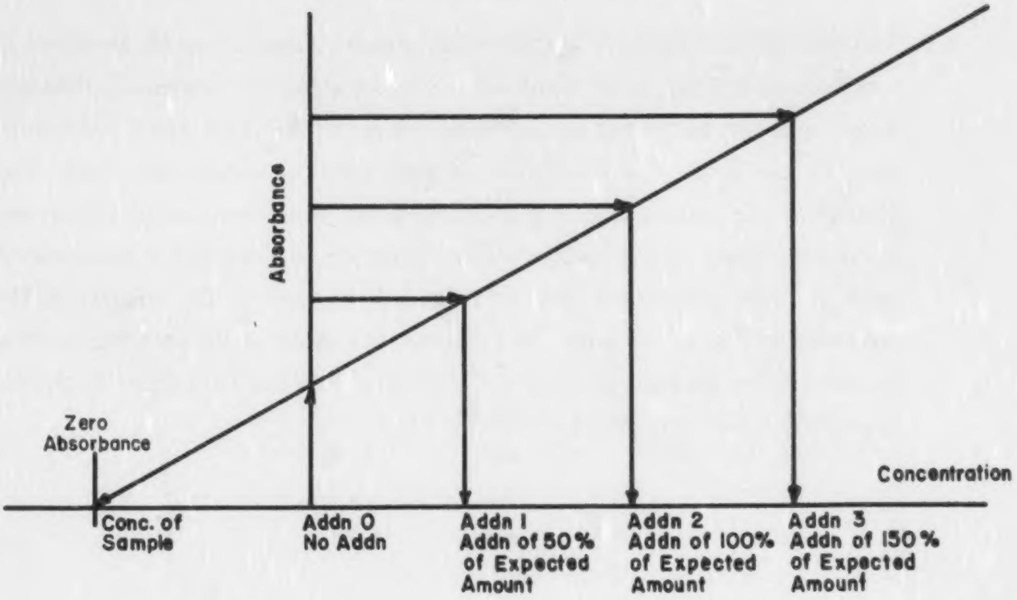

Absorbance
Concentration
Zero Absorbance
Conc. of Sample
Addn 0 No Addn
Addn 1 Addn of 50% of Expected Amount
Addn 2 Addn of 100% of Expected Amount
Addn 3 Addn of 150% of Expected Amount

FIGURE 1. STANDARD ADDITION PLOT

9. General Procedure for Analysis by Atomic Absorption

9.1 Differences between the various makes and models of satisfactory atomic absorption spectrophotometers prevent the formulation of detailed instructions applicable to every instrument. The analyst should follow the manufacturer's operating instructions for his particular instrument. In general, after choosing the proper hollow cathode lamp for the analysis, the lamp should be allowed to warm up for a minimum of 15 minutes. During this period, align the instrument, position the monochromator at the correct wavelength, select the proper monochromator slit width, and adjust the hollow cathode current according to the manufacturer's recommendation. Subsequently, light the flame and regulate the flow of fuel and oxidant, adjust the burner and nebulizer flow rate for maximum percent absorption and stability, and balance the photometer. Run a series of standards of the element under analysis and construct working curves by plotting the concentrations of the standards against the absorbance. For those instruments which read directly in concentration set the curve corrector to read out the proper concentration. Aspirate the samples and determine the concentrations either directly or from the calibration curve. For best results run standards each time a sample or series of samples are run.

9.2 Special Extraction Procedure: When the concentration of the metal is not sufficiently high to determine directly, or when considerable dissolved solids are present in the sample, certain of the metals may be chelated and extracted with organic solvents. Ammonium pyrrolidine dithiocarbamate (APDC) in methyl isobutyl ketone (MIBK) is widely used for this purpose and is particularly useful for zinc, cadmium, iron, manganese, copper, silver, lead and chromium^{+6}. Tri-valent chromium does not react with APDC unless it has first been converted to the hexavalent form [Atomic Absorption Newsletter *6*, p 128 (1967)]. Aluminum, beryllium, barium and strontium also do not react with APDC. While the APDC-MIBK chelating-solvent system can be used satisfactorily, it is possible to experience difficulties. Also, when multiple metals are to be determined either larger sample volumes must be extracted or individual extractions made for each metal being determined. The acid form of APDC-pyrrolidine dithiocarbamic acid prepared directly in chloroform as described by Lakanen, [Atomic Absorption Newsletter 5, p 17 (1966)], has been found to be most advantageous. It is very stable and may be stored in a brown bottle in the refrigerator for months. Because chloroform is used as the solvent, it may not be aspirated into the flame. The following procedure is suggested.

9.2.1 Extraction Procedure with pyrrolidine dithiocarbamic acid (PDCA) in chloroform.

a. Transfer 200 ml of sample into a 250 ml separatory funnel, add 2 drops bromphenol blue indicator solution (7.7.3) and mix.

b. Prepare a blank and sufficient standards in the same manner and adjust the volume of each to approximately 200 ml with deionized distilled water. All of the metals to be determined may be combined into single solutions at the appropriate concentration levels.

c. Adjust the pH by addition of 2N NH_4OH solution (7.7.2) until a blue color persists. Add HCl (7.7.4) dropwise until the blue color just disappears; then add 2.0 ml HCl (7.7.4) in excess. The pH at this point should be 2.3. (The pH adjustment may be made with a pH meter instead of using indicator).

d. Add 5 ml of PDCA-chloroform reagent (7.7.1) and shake vigorously for 2 minutes. Allow the phases to separate and drain the chloroform layer into a 100 ml beaker.

e. Add a second portion of 5 ml PDCA-chloroform reagent (7.7.1) and shake vigorously for 2 minutes. Allow the phases to separate and combine the chloroform phase with that obtained in step (d).

f. Determine the pH of the aqueous phase and adjust to 4.5.

g. Repeat step (d) again combining the solvent extracts.

h. Readjust the pH to 5.5, extract, readjust to 6.5 and extract a fifth time. Combine all extracts and evaporate to dryness on a steam bath.

i. Hold the beaker at a 45 degree angle, and slowly add 2 ml of conc. distilled nitric acid, rotating the beaker to effect thorough contact of the acid with the residue.

j. Place the beaker on a low temperature hotplate and evaporate just to dryness.

k. Add 2 ml of nitric acid (1:1) to the beaker and heat for 1 minute. Cool, quantitatively transfer the solution to a 10 ml volumetric flask and bring to volume with distilled water. The sample is now ready for analysis.

9.3 General-purpose electrically heated devices (flameless atomization) have recently been introduced as a means of extending detection limits. These techniques are generally acceptable but the analyst should be cautioned as to possible suppression or enhancement effects. With flameless atomization, background correction becomes of high importance. This is because certain samples, when atomized, may absorb or scatter light from the hollow cathode lamp. It can be caused by the presence of gaseous molecular species, salt particles, or smoke in the sample beam. If no correction is made, sample absorbance will be greater than it should be, and the analytical result will be erroneously high.

10. Calculation

10.1 Direct determination of liquid samples: Read the metal value in mg/l from the calibration curve or directly from the readout system of the instrument.

10.1.1 If dilution of sample was required:

$$\text{mg/l metal in sample} = (\text{mg/l of metal in the diluted aliquot}) \times D$$

$$\text{where } D = \frac{\left(\begin{array}{c}\text{ml of}\\ \text{aliquot}\end{array}\right) + \left(\begin{array}{c}\text{ml of deionized}\\ \text{distilled water}\end{array}\right)}{\text{ml of aliquot}}$$

10.2 For samples containing particulates:

$$\text{mg/l metal in sample} = \frac{A \times B}{C}$$

where:

A = mg/l of metal in processed sample

B = final volume of processed sample in ml

C = volume of sample aliquot processed in ml

10.3 For solid samples: Report all concentrations as mg/kg dry weight.

10.3.1 Dry sample

$$\text{mg/kg} = \frac{\left(\begin{array}{c}\text{mg/l of constituent}\\ \text{in prepared sample}\end{array}\right) \times \left(\begin{array}{c}\text{volume of prepared}\\ \text{sample in ml}\end{array}\right)}{\text{weight of dry sample in g}}$$

10.3.2 Wet sample

$$\text{mg/kg} = \frac{\left(\begin{array}{c}\text{mg/l of constituent}\\ \text{in prepared sample}\end{array}\right) \times \left(\begin{array}{c}\text{volume of prepared}\\ \text{sample in ml}\end{array}\right)}{(\text{weight of wet sample in g}) \times (\text{\% solids})}$$

ALUMINUM

(Standard Conditions)

STORET NO. Total 01105

Optimum Concentration Range: 5-100 mg/l using a wavelength of 309.2 nm

Sensitivity: 1.0 mg/l

Detection Limit: 0.1 mg/l

Preparation of Standard Solution

1. Stock Solution: Carefully weigh 1.000 gram of aluminum metal (analytical reagent grade). Add 15 ml of conc. HCl to the metal in a covered beaker and warm gently. When solution is complete, transfer quantitatively to a 1 liter volumetric flask and make up to volume with deionized distilled water. 1 ml = 1 mg Al (1000 mg/l).
2. Potassium Chloride Solution: Dissolve 95 g potassium chloride (KCl) in deionized distilled water and make up to 1 liter.
3. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The *calibration standards* should be prepared using the same type of acid (HCl or HNO_3) and at the same concentration as the samples for analysis. To each 100 ml of standard and sample alike add 2.0 ml potassium chloride solution.

Sample Preparation

1. The procedure for the determination of total metals as given in part 4.1.3 of the Atomic Absorption Methods section of this manual has been found to be satisfactory.

Instrumental Parameters (General)

1. Aluminum hollow cathode lamp
2. Wavelength: 309.2 nm
3. Fuel: Acetylene
4. Oxidant: Nitrous oxide
5. Type of flame: Fuel rich

Interferences

1. Aluminum is partially ionized in the nitrous oxide-acetylene flame. This problem may be controlled by the addition of an alkali metal (potassium, 1000 μg/ml) to both sample and standard solutions.

Notes

1. The following lines may also be used:
   308.2 nm Relative Sensitivity 1
   396.2 nm Relative Sensitivity 2
   394.4 nm Relative Sensitivity 2.5
2. Data to be entered into STORET must be reported as μg/l.
3. For concentrations of aluminum below 0.3 mg/l, the Eriochrome cyanine R method may be used (Standard Methods, 13th Edition, p 57).

Precision and Accuracy

1. An interlaboratory study on trace metal analyses by atomic absorption was conducted by the Quality Assurance and Laboratory Evaluation Branch of MDQARL. Six synthetic concentrates containing varying levels of aluminum, cadmium, chromium, copper, iron, manganese, lead and zinc were added to natural water samples. The statistical results for aluminum were as follows:

Number of Labs	True values μg/liter	Mean Value μg/liter	Standard Deviation μg/liter	Accuracy as % Bias
38	1205	1281	299	6.3
38	1004	1003	391	–0.1
37	500	463	202	–7.4
37	625	582	272	–6.8
22	35	96	108	175
21	15	109	168	626

ANTIMONY

(Standard Conditions)

STORET NO. Total 01097

Optimum Concentration Range: 1-40 mg/l using a wavelength of 217.6 nm

Sensitivity: 0.5 mg/l

Detection Limit: 0.2 mg/l

Preparation of Standard Solution

1. Stock Solution: Carefully weigh 2.7426 g of antimony potassium tartrate (analytical reagent grade) and dissolve in deionized distilled water. Dilute to 1 liter with deionized distilled water. 1 ml = 1 mg Sb (1000 mg/l).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The *calibration standards* should be prepared using the same type of acid (HCl or HNO_3) and at the same concentration as the samples for analysis.

Sample Preparation

1. The procedure for the determination of total metals as given in part 4.1.3 of the Atomic Absorption Methods section of this manual has been found to be satisfactory.

Instrumental Parameters (General)

1. Antimony hollow cathode lamp
2. Wavelength: 217.6 nm
3. Fuel: Acetylene
4. Oxidant: Air
5. Type of flame: Fuel lean

Interferences

1. In the presence of lead (1000 mg/l), a spectral interference may occur at the 217.6 nm resonance line. In this case the 231.1 nm antimony line should be used.
2. Increasing acid concentrations decrease antimony absorption. To avoid this effect, the acid concentration in the samples and in the standards should be matched.

Notes

1. Data to be entered into STORET must be reported as µg/l.

Precision and Accuracy

1. In a single laboratory (MDQARL), using a mixed industrial-domestic waste effluent at concentrations of 5.0 and 15 mg Sb/1, the standard deviations were ±0.08 and ±0.1, respectively. Recoveries at these levels were 96% and 97%, respectively.

ARSENIC

(Gaseous Hydride Method)

STORET NO. Total 01002

1. Scope and Application

   1.1 The gaseous hydride method determines inorganic arsenic when present in concentrations at or above 2 μg/l. The method is applicable to most fresh and saline waters in the absence of high concentrations of chromium, cobalt, copper, mercury, molybdenum, nickel and silver.

2. Summary of Method

   2.1 Arsenic in the sample is first reduced to the trivalent form using $SnCl_2$ and converted to arsine, AsH_3, using zinc metal. The gaseous hydride is swept into an argon-hydrogen flame of an atomic absorption spectrophotometer. The working range of the method is 2-20 μg/l. The 193.7 nm wavelength line is used.

3. Comments

   3.1 In analyzing most surface and ground waters, interferences are rarely encountered. Industrial waste samples should be spiked with a known amount of arsenic to establish adequate recovery.

   3.2 Organic forms of arsenic must be converted to inorganic compounds and organic matter must be oxidized before beginning the analysis. The oxidation procedure given in Standard Methods, 13th Edition, Method 104B, p 65, Procedure 4.a has been found suitable.

   3.3 The silver diethyldithiocarbamate colorimetric procedure may also be used (Standard Methods, 13th Edition, p 62) with the digestion described in (3.2). l-Ephedrine in chloroform has been found to be a suitable solvent for silver diethyldithiocarbamate if the analyst finds the odor of pyridine objectionable [Anal. Chem. *45*, 1786 (1973)].

   3.4 Data to be entered into STORET must be reported as μg/l.

4. Precision and Accuracy

   4.1 Ten replicate solutions of o-arsenilic acid at the 5, 10 and 20 μg/l level were analyzed by a single laboratory (Caldwell, et. al.). Standard deviations were ±0.3, ±0.9 and ±1.1 with recoveries of 94, 93 and 85%, respectively.

Bibliography

1. Caldwell, J. S., Lishka, R. J., and McFarren, E. F., "Evaluation of a Low Cost Arsenic and Selenium Determination at Microgram per Liter Levels", JAWWA., vol 65, p 731, Nov., 1973.

BARIUM

(Standard Conditions)

STORET NO. Total 01007

Optimum Concentration Range: 1-20 mg/l using a wavelength of 553.6 nm

Sensitivity: 0.4 mg/l

Detection Limit: 0.03 mg/l

Preparation of Standard Solution

1. Stock Solution: Dissolve 1.7787 g barium chloride ($BaCl_2 \cdot 2H_2O$, analytical reagent grade) in deionized distilled water and dilute to 1 liter.
   1 ml = 1 mg Ba (1000 mg/l).
2. Potassium chloride solution: Dissolve 95 g potassium chloride, KCl, in deionized distilled water and make up to 1 liter.
3. Prepare dilutions of the stock barium solution to be used as calibration standards at the time of analysis. To each 100 ml of standard and sample alike add 2.0 ml potassium chloride solution. The *calibration standards* should be prepared using the same type of acid (HCl or HNO_3) and at the same concentration as the samples for analysis.

Sample Preparation

1. The procedure for the determination of total metals as given in part 4.1.3 of the Atomic Absorption Methods section of this manual has been found to be satisfactory.

Instrumental Parameters (General)

1. Barium hollow cathode lamp
2. Wavelength: 553.6 nm
3. Fuel: Acetylene
4. Oxidant: Nitrous oxide
5. Type of flame: Fuel rich

Interferences

1. The use of a nitrous oxide-acetylene flame virtually eliminates chemical interference; however, barium is easily ionized in this flame and potassium must be added (1000 mg/l) to standards and samples alike to control this effect.
2. If the nitrous oxide flame is not available and acetylene-air is used, phosphate, silicon and aluminum will severely depress the barium absorbance. This may be overcome by the addition of 2000 mg/l lanthanum.

Notes

1. Data to be entered into STORET must be reported as μg/l.

Precision and Accuracy

1. In a single laboratory (MDQARL), using a mixed industrial-domestic waste effluent at concentrations of 0.40 and 2.0 mg Ba/l, the standard deviations were ±0.043 and ±0.13, respectively. Recoveries at these levels were 94% and 113%, respectively.

BERYLLIUM

(Standard Conditions)

STORET NO. Total 01012

Optimum Concentration Range: 0.05-2 mg/l using a wavelength of 234.9 nm

Sensitivity: 0.025 mg/l

Detection Limit: 0.005 mg/l

Preparation of Standard Solution

1. Stock solution: Dissolve 11.6586 g beryllium sulfate, $BeSO_4$, in deionized distilled water containing 2 ml conc. nitric acid and dilute to 1 liter. 1 ml = 1 mg Be (1000 mg/l).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The *calibration standards* should be prepared using the same type of acid (HCl or HNO_3) and at the same concentration as the samples for analysis.

Sample Preparation

1. The procedure for the determination of total metals as given in part 4.1.3 of the Atomic Absorption Methods section of this manual has been found to be satisfactory.

Instrumental Parameters (General)

1. Beryllium hollow cathode lamp
2. Wavelength: 234.9 nm
3. Fuel: Acetylene
4. Oxidant: Nitrous oxide
5. Type of flame: Fuel rich

Interferences:

1. Sodium and silicon at concentrations in excess of 1000 mg/l have been found to severely depress the beryllium absorbance.
2. Bicarbonate ion is reported to interfere; however, its effect is eliminated when samples are acidified to a pH of 1.5.
3. Aluminum at concentrations of >500 µg/l is reported to depress the sensitivity of beryllium [Spectrochim Acta *22*, 1325 (1966)].

Notes

1. Data to be entered into STORET must be reported as µg/l.
2. The "aluminon method" may also be used (Standard Methods, 13th Edition, p 67).

Precision and Accuracy

1. In a single laboratory (MDQARL), using a mixed industrial-domestic waste effluent at concentrations of 0.01, 0.05 and 0.25 mg Be/l, the standard deviations were ±0.001, ±0.001 and ±0.002, respectively. Recoveries at these levels were 100%, 98% and 97%, respectively.

CADMIUM

(Standard Conditions)

STORET NO. Total 01027

Optimum Concentration Range: 0.05-2 mg/l using a wavelength of 228.8 nm

Sensitivity: 0.025 mg/l

Detection Limit: 0.002 mg/l

Preparation of Standard Solution

1. Stock Solution: Carefully weigh 2.282 g of cadmium sulfate ($CdSO_4 \cdot 8H_2O$, analytical reagent grade) and dissolve in deionized distilled water. 1 ml = 1 mg Cd (1000 mg/l).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The *calibration standards* should be prepared using the same type of acid (HCl or HNO_3) and at the same concentration as the samples for analysis.

Sample Preparation

1. The procedure for the determination of total metals as given in part 4.1.3 of the Atomic Absorption Methods section of this manual has been found to be satisfactory.

Instrumental Parameters (General)

1. Cadmium hollow cathode lamp
2. Wavelength: 228.8 nm
3. Fuel: Acetylene
4. Oxidant: Air
5. Type of flame: Oxidizing

Notes

1. For levels of cadmium below 20 µg/l, the extraction procedure is recommended.
2. Data to be entered into STORET must be reported as µg/l.
3. The dithizone colorimetric procedure may be used (Standard Methods, 13th Edition, p 422).

Precision and Accuracy

1. An interlaboratory study on trace metal analyses by atomic absorption was conducted by the Quality Assurance and Laboratory Evaluation Branch of MDQARL. Six synthetic concentrates containing varying levels of aluminum, cadmium, chromium, copper, iron, manganese, lead and zinc were added to natural water samples. The statistical results for cadmium were as follows:

Number of Labs	True Values µg/liter	Mean Value µg/liter	Standard Deviation µg/liter	Accuracy as % Bias
74	71	70	21	−2.2
73	78	74	18	−5.7
63	14	16.8	11.0	19.8
68	18	18.3	10.3	1.9
55	1.4	3.3	5.0	135
51	2.8	2.9	2.8	4.7

CALCIUM

(Standard Conditions)

STORET NO. Total 00916

Optimum Concentration Range: 0.2-20 mg/l using a wavelength of 422.7 nm

Sensitivity: 0.08 mg/l

Detection Limit: 0.003 mg/l

Preparation of Standard Solution

1. Stock Solution: Suspend 1.250 g of $CaCO_3$ (analytical reagent grade), dried at 180°C for 1 hour before weighing, in deionized distilled water and dissolve cautiously with a minimum of dilute HCl. Dilute to 1000 ml with deionized distilled water. 1 ml = 0.5 mg Ca (500 mg/l).
2. Lanthanum chloride solution: Dissolve 29 g of La_2O_3, slowly and in small portions, in 250 ml conc. HCl (*Caution*: Reaction is violent) and dilute to 500 ml with deionized distilled water.
3. Prepare dilutions of the stock calcium solutions to be used as calibration standards at the time of analysis. To each *calibration standard* solution, add 1.0 ml of $LaCl_3$ solution for each 10 ml of volume of working standard, ie., 20 ml working standard + 2 ml $LaCl_3$ = 22 ml.

Sample Preparation

1. For the analysis of total calcium in domestic and industrial effluents, the procedure for the determination of total metals as given in part 4.1.3 of the Atomic Absorption Methods section of this manual has been found to be satisfactory.
2. For ambient waters, a representative aliquot of a well-mixed sample may be used directly for analysis. If suspended solids are present in sufficient amounts to clog the nebulizer, the sample may be allowed to settle and the supernatant liquid analyzed directly.

Instrumental Parameters (General)

1. Calcium hollow cathode lamp
2. Wavelength: 422.7 nm
3. Fuel: Acetylene
4. Oxidant: Air
5. Type of flame: Reducing

Notes

1. Phosphate, sulfate and aluminum interfere but are masked by the addition of lanthanum. Since low calcium values result if the pH of the sample is above 7, both standards and samples are prepared in dilute hydrochloric acid solution. Concentrations of magnesium greater than 1000 mg/l also cause low calcium values. Concentrations of up to 500 mg/l each of sodium, potassium and nitrate cause no interference.
2. Anionic chemical interferences can be expected if lanthanum is not used in samples and standards.
3. The nitrous oxide-acetylene flame will provide two to five times greater sensitivity and freedom from chemical interferences. Ionization interferences should be controlled by adding a large amount of alkali to the sample and standards. The analysis appears to be free from chemical suppressions in the nitrous oxide-acetylene flame. (Atomic Absorption Newsletter *14*, 29 [1975]).
4. The 239.9 nm line may also be used. This line has a sensitivity of 20 mg/l.
5. Data to be entered into STORET must be reported as mg/l.
6. The EDTA titrimetric method may be used (Standard Methods, 13th Edition, p 84).

Precision and Accuracy

1. In a single laboratory (MDQARL), using distilled water at concentrations of 9.0 and 36 mg/l, the standard deviations were ±0.3 and ±0.6, respectively. Recoveries at both these levels were 99%.

CHROMIUM

(Standard Conditions)

.STORET NO. Total 01034

Optimum Concentration Range: 0.2-10 mg/l using a wavelength of 357.9 nm

Sensitivity: 0.1 mg/l

Detection Limit: 0.02 mg/l

Preparation of Standard Solution

1. Stock Solution: Dissolve 1.923 g of chromium trioxide (CrO_3, reagent grade) in deionized distilled water. When solution is complete, acidify with redistilled HNO_3 and dilute to 1 liter with deionized distilled water. 1 ml = 1 mg Cr (1000 mg/l).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The *calibration standards* should be prepared using the same type of acid (HCl or HNO_3) and at the same concentration as the samples for analysis.

Sample Preparation

1. The procedure for the determination of total metals as given in part 4.1.3 of the Atomic Absorption Methods section of this manual has been found to be satisfactory.

Instrumental Parameters (General)

1. Chromium hollow cathode lamp
2. Wavelength: 357.9 nm
3. Fuel: Acetylene
4. Oxidant: Air
5. Type of flame: Slightly fuel rich

Notes

1. The following wavelengths may also be used:
   360.5 nm Relative Sensitivity 1.2
   359.3 nm Relative Sensitivity 1.4
   425.4 nm Relative Sensitivity 2
   427.5 nm Relative Sensitivity 3
   428.9 nm Relative Sensitivity 4
2. The nitrous oxide-acetylene flame provides greater freedom from chemical and matrix interference.

3. The absorption of chromium is suppressed by iron and nickel. If the analysis is performed in a lean flame the interference can be lessened but the sensitivity will also be reduced. The interference does not exist in a nitrous oxide-acetylene flame.
4. The suppression of both Cr (III) and Cr (VI) absorption by most interfering ions in fuel rich air-acetylene flames is reportedly controlled by the addition of 1% ammonium bifluoride in 0.2% sodium sulfate [Talanta *20*, 631 (1973)] or 1% oxine.
5. For levels of chromium below 50 μg/1, the extraction procedure is recommended. Only hexavalent chromium will react with APDC, thus, to measure trivalent chromium an oxidation step must be included. [Atomic Absorption Newsletter, *6*, p 128 (1967)].
6. Data to be entered into STORET must be reported as μg/1.
7. The diphenylcarbazide colorimetric procedure may be used (Standard Methods, 13th Edition, p 426).

Precision and Accuracy

1. An interlaboratory study on trace metal analyses by atomic absorption was conducted by the Quality Assurance and Laboratory Evaluation Branch of MDQARL. Six synthetic concentrates containing varying levels of aluminum, cadmium, chromium, copper, iron, manganese, lead and zinc were added to natural water samples. The statistical results for chromium were as follows:

Number of Labs	True Values μg/liter	Mean Value μg/liter	Standard Deviation μg/liter	Accuracy as % Bias
74	370	353	105	–4.5
76	407	380	128	–6.5
72	74	72	29	–3.1
70	93	84	35	–10.2
47	7.4	10.2	7.8	37.7
47	15.0	16.0	9.0	6.8

COBALT

(Standard Conditions)

STORET NO. Total 01037

Optimum Concentration Range: 0.5-10 mg/l using a wavelength of 240.7 nm

Sensitivity: 0.2 mg/l

Detection Limit: 0.03 mg/l

Preparation of Standard Solution

1. Stock Solution: Dissolve 4.307 g of cobaltous chloride, $CoCl_2 \cdot 6H_2O$ (analytical reagent grade), in deionized distilled water. Add 10 ml of concentrated nitric acid and dilute to 1 liter with deionized distilled water. 1 ml = 1 mg Co (1000 mg/l).

2. Prepare dilutions of the stock cobalt solution to be used as calibration standards at the time of analysis. The *calibration standards* should be prepared using the same type of acid (HCl or HNO_3) and at the same concentration as the samples for analysis.

Sample Preparation

1. The procedure for the determination of total metals as given in part 4.1.3 of the Atomic Absorption Methods section of this manual has been found to be satisfactory.

Instrumental Parameters (General)

1. Cobalt hollow cathode lamp
2. Wavelength: 240.7 nm
3. Fuel: Acetylene
4. Oxidant: Air
5. Type of Flame: Oxidizing

Notes

1. For levels of cobalt below 50 µg/l, the extraction procedure is recommended.
2. Data to be entered into STORET must be reported as µg/l.

Precision and Accuracy

1. In a single laboratory (MDQARL), using a mixed industrial-domestic waste effluent at concentrations of 0.20, 1.0 and 5.0 mg Co/l, the standard deviations were ±0.013, ±0.1 and ±0.05, respectively. Recoveries at these levels were 98%, 98% and 97%, respectively.

COPPER

(Standard Conditions)

STORET NO. Total 01042

Optimum Concentration Range: 0.2-10 mg/l using a wavelength of 324.7 nm

Sensitivity: 0.1 mg/l

Detection Limit: 0.01 mg/l

Preparation of Standard Solution

1. Stock Solution: Carefully weigh 1.00 g of electrolyte copper (analytical reagent grade). Dissolve in 5 ml redistilled HNO_3 and make up to 1 liter with deionized distilled water. Final concentration is 1 mg Cu per ml (1000 mg/1).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The *calibration standards* should be prepared using the same type of acid (HCl or HNO_3) and at the same concentration as the samples for analysis.

Sample Preparation

1. The procedure for the determination of total metals as given in part 4.1.3 of the Atomic Absorption Methods section of this manual has been found to be satisfactory.

Instrumental Parameters (General)

1. Copper hollow cathode lamp
2. Wavelength: 324.7 nm
3. Fuel: Acetylene
4. Oxidant: Air
5. Type of flame: Oxidizing

Notes

1. For levels of copper below 20 μg/l, the extraction procedure is recommended.
2. Copper atoms are distributed over a wider area in laminar flow-flames than that normally found. Consequently, the burner parameters are not as critical as for most other elemental determinations.
3. Because of the spectral intensity of the 324.7 nm line, the P.M. tube may become saturated. If this situation occurs the current should be decreased.
4. Numerous absorption lines are available for the determination of copper. By selecting a suitable absorption wavelength, copper samples may be analyzed over a very wide range of concentration. The following lines may be used:
   327.4 nm Relative Sensitivity 2

217.8 nm Relative Sensitivity 4
216.5 nm Relative Sensitivity 7
218.1 nm Relative Sensitivity 9
222.5 nm Relative Sensitivity 20
249.2 nm Relative Sensitivity 90

5. Data to be entered into STORET must be reported as µg/l.
6. The 2,9-dimethyl-1, 10-phenanthroline colorimetric method may be used (Standard Methods, 13th Edition, p. 430).

Precision and Accuracy

1. An interlaboratory study on trace metal analyses by atomic absorption was conducted by the Quality Assurance and Laboratory Evaluation Branch of MDQARL. Six synthetic concentrates containing varying levels of aluminum, cadmium, chromium, copper, iron, manganese, lead and zinc were added to natural water samples. The statistical results for copper were as follows:

Number of Labs	True Values µg/liter	Mean Value µg/liter	Standard Deviation µg/liter	Accuracy as % Bias
91	302	305	56	0.9
92	332	324	56	−2.4
86	60	64	23	7.0
84	75	76	22	1.3
66	7.5	9.7	6.1	29.7
66	12.0	13.9	9.7	15.5

IRON

(Standard Conditions)

STORET NO. Total 01045

Optimum Concentration Range: 0.3-10 mg/l using a wavelength of 248.3 nm

Sensitivity: 0.12 mg/l

Detection Limit: 0.02 mg/l

Preparation of Standard Solution

1. Stock Solution: Carefully weigh 1.000 g of pure iron wire (analytical reagent grade) and dissolve in 5 ml redistilled HNO_3, warming if necessary. When solution is complete make up to 1 liter with deionized distilled water. 1 ml = 1 mg Fe (1000 mg/l).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The *calibration standards* should be prepared using the same type of acid (HCl or HNO_3) and at the same concentration as the samples for analysis.

Sample Preparation

1. The procedure for the determination of total metals as given in part 4.1.3 of the Atomic Absorption Methods section of this manual has been found to be satisfactory.

Instrumental Parameters (General)

1. Iron hollow cathode lamp
2. Wavelength: 248.3 nm
3. Fuel: Acetylene
4. Oxidant: Air
5. Type of flame: Oxidizing

Notes

1. The following lines may also be used:
   248.8 nm Relative Sensitivity 2
   271.9 nm Relative Sensitivity 4
   302.1 nm Relative Sensitivity 5
   252.7 nm Relative Sensitivity 6
   372.0 nm Relative Sensitivity 10
   386.0 nm Relative Sensitivity 20
   344.1 nm Relative Sensitivity 30
2. Absorption is strongly dependent upon the lamp current.

3. Better signal-to-noise can be obtained from a neon-filled hollow cathode lamp than an argon filled lamp.
4. Data to be reported into STORET must be reported as μg/l.
5. The 1,10-phenanthroline colorimetric method may be used (Standard Methods, 13th Edition, p 433).

Precision and Accuracy

1. An interlaboratory study on trace metal analyses by atomic absorption was conducted by the Quality Assurance and Laboratory Evaluation Branch of MDQARL. Six synthetic concentrates containing varying levels of aluminum, cadmium, chromium, copper, iron, manganese, lead and zinc were added to natural water samples. The statistical results for iron were as follows:

Number of Labs	True Values μg/liter	Mean Value μg/liter	Standard Deviation μg/liter	Accuracy as % Bias
82	840	855	173	1.8
85	700	680	178	–2.8
78	350	348	131	–0.5
79	438	435	183	–0.7
57	24	58	69	141
54	10	48	69	382

LEAD

(Standard Conditions)

STORET NO. Total 01051

Optimum Concentration Range: 1-20 mg/l using a wavelength of 283.3 nm

Sensitivity: 0.5 mg/l

Detection Limit: 0.05 mg/l

Preparation of Standard Solution

1. Stock Solution: Carefully weigh 1.599 g of lead nitrate, $Pb(NO_3)_2$ (analytical reagent grade), and dissolve in deionized distilled water. When solution is complete acidify with 10 ml redistilled HNO_3 and dilute to 1 liter with deionized distilled water. 1 ml = 1 mg Pb (1000 mg/l).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The *calibration standards* should be prepared using the same type of acid (HCl or HNO_3) and at the same concentration as the samples for analysis.

Sample Preparation

1. The procedure for the determination of total metals as given in part 4.1.3 of the Atomic Absorption Methods section of this manual has been found to be satisfactory.

Instrumental Parameters (General)

1. Lead hollow cathode lamp
2. Wavelength: 283.3 nm
3. Fuel: Acetylene
4. Oxidant: Air
5. Type of flame: Slightly oxidizing

Notes

1. The analysis of this metal is exceptionally sensitive to turbulence and absorption bands in the flame. Therefore, some care should be taken to position the light beam in the most stable, center portion of the flame. To do this, first adjust the burner to maximize the absorbance reading with a lead standard. Then, aspirate a water blank and make minute adjustments in the burner alignment to minimize the signal.
2. For levels of lead below 100 μg/l, the extraction procedure is recommended. The optimum pH for the extraction of lead is 2.8.

3. The following lines may also be used:
   217.0 nm Relative Sensitivity 0.4
   261.4 nm Relative Sensitivity 30
4. Data to be entered into STORET must be reported as μg/l.
5. The dithizone colorimetric method may be used (Standard Methods, 13th Edition, p 436).

Precision and Accuracy

1. An interlaboratory study on trace metal analyses by atomic absorption was conducted by the Quality Assurance and Laboratory Evaluation Branch of MDQARL. Six synthetic concentrates containing varying levels of aluminum, cadmium, chromium, copper, iron, manganese, lead and zinc were added to natural water samples. The statistical results for lead were as follows:

Number of Labs	True Values μg/liter	Mean Value μg/liter	Standard Deviation μg/liter	Accuracy as % Bias
74	367	377	128	2.9
74	334	340	111	1.8
64	101	101	46	–0.2
64	84	85	40	1.1
61	37	41	25	9.6
60	25	31	22	25.7

MAGNESIUM

(Standard Conditions)

STORET NO. Total 00927

Optimum Concentration Range: 0.02-2 mg/l using a wavelength of 285.2 nm

Sensitivity: 0.007 mg/l

Detection Limit: 0.0005 mg/l

Preparation of Standard Solution

1. Stock Solution: Dissolve 0.829 g of magnesium oxide, MgO (analytical reagent grade), in 10 ml of redistilled HNO_3 and dilute to 1 liter with deionized distilled water. 1 ml = 0.50 mg Mg (500 mg/l).
2. Lanthanum chloride solution: Dissolve 29 g of La_2O_3, slowly and in small portions in 250 ml conc. HCl, (*Caution*: Reaction is violent) and dilute to 500 ml with deionized distilled water.
3. Prepare dilutions of the stock magnesium solution to be used as calibration standards at the time of analysis. To each *calibration standard* solution, add 1.0 ml of $LaCl_3$ solution for each 10 ml of volume of working standard, ie., 20 ml working standard + 2 ml $LaCl_3$ = 22 ml.

Sample Preparation

1. For the analysis of total magnesium in domestic and industrial effluents, the procedure for the determination of total metals as given in part 4.1.3 of the Atomic Absorption Methods section of this manual has been found to be satisfactory.
2. For ambient waters, a representative aliquot of a well-mixed sample may be used directly for analysis. If suspended solids are present in sufficient amounts to clog the nebulizer, the sample may be allowed to settle and the supernatant liquid analyzed directly.
3. Samples should be preserved with (1:1) nitric acid to a pH of 2 at the time of collection.

Instrumental Parameters (General)

1. Magnesium hollow cathode lamp
2. Wavelength: 285.2 nm
3. Fuel: Acetylene
4. Oxidant: Air
5. Type of flame: Reducing

Notes

1. Analytical sensitivity decreases with increased lamp current.
2. The interference caused by aluminum at concentrations greater than 2 mg/l is masked by addition of lanthanum. Sodium, potassium and calcium cause no interference at concentrations less than 400 mg/l.
3. Because of the spectral intensity of the 285.2 nm line, the P.M. tube may become saturated. If this situation occurs, the current should be decreased.
4. The following line may also be used:
   202.5 nm Relative Sensitivity 25
5. To cover the range of magnesium values normally observed in surface waters (0.1-20 mg/l), it is suggested that the burner be rotated 55°.
6. Data to be entered into STORET must be reported as mg/l.
7. The gravimetric method may be used (Standard Methods, 13th Edition, p 201).

Precision and Accuracy

1. In a single laboratory (MDQARL), using a distilled water sample at concentrations of 2.1 and 8.2 mg/l, the standard deviations were ±0.1 and ±0.2, respectively. Recoveries at both of these levels were 100%.

MANGANESE

(Standard Conditions)

STORET NO. Total 01055

Optimum Concentration Range: 0.1-10 mg/l using a wavelength of 279.5 nm

Sensitivity: 0.05 mg/l

Detection Limit: 0.01 mg/l

Preparation of Standard Solution

1. Stock Solution: Carefully weigh 1.000 g of manganese metal (analytical reagent grade) and dissolve in 10 ml of redistilled HNO_3. When solution is complete dilute to 1 liter with 1% (V/V) HCl. 1 ml = 1 mg Mn (1000 mg/1).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The *calibration standards* should be prepared using the same type of acid (HCl or HNO_3) and at the same concentration as the samples for analysis.

Sample Preparation

1. The procedure for the determination of total metals as given in part 4.1.3 of the Atomic Absorption Methods section of this manual has been found to be satisfactory.

Instrumental Parameters (General)

1. Manganese hollow cathode lamp
2. Wavelength: 279.5 nm
3. Fuel: Acetylene
4. Oxidant: Air
5. Type of flame: Oxidizing

Notes

1. For levels of manganese below 25 μg/l, the extraction procedure is recommended. The extraction is carried out at a pH of 4.5 to 5. The manganese chelate is very unstable and the analysis must be made without delay to prevent its re-solution in the aqueous phase.
2. Analytical sensitivity is somewhat dependent on lamp current.
3. The following line may also be used:
   403.1 nm Relative Sensitivity 10.
4. Data to be entered into STORET must be reported as μg/l.

Precision and Accuracy

1. An interlaboratory study on trace metal analyses by atomic absorption was conducted by the Quality Assurance and Laboratory Evaluation Branch of MDQARL. Six synthetic concentrates containing varying levels of aluminum, cadmium, chromium, copper, iron, manganese, lead and zinc were added to natural water samples. The statistical results for manganese were as follows:

Number of Labs	True Values μg/liter	Mean Value μg/liter	Standard Deviation μg/liter	Accuracy as % Bias
77	426	432	70	1.5
78	469	474	97	1.2
71	84	86	26	2.1
70	106	104	31	−2.1
55	11	21	27	93
55	17	21	20	22

MERCURY IN WATER

(Manual Cold Vapor Technique)

STORET NO. Total 71900

1. Scope and Application

1.1 This method is applicable to drinking, surface, and saline waters, domestic and industrial wastes.

1.2 In addition to inorganic forms of mercury, organic mercurials may also be present. These organo-mercury compounds will not respond to the flameless atomic absorption technique unless they are first broken down and converted to mercuric ions. Potassium permanganate oxidizes many of these compounds, but recent studies have shown that a number of organic mercurials, including phenyl mercuric acetate and methyl mercuric chloride, are only partially oxidized by this reagent. Potassium persulfate has been found to give approximately 100% recovery when used as the oxidant with these compounds. Therefore, a persulfate oxidation step following the addition of the permanganate has been included to insure that organomercury compounds, if present, will be oxidized to the mercuric ion before measurement. A heat step is required for methyl mercuric chloride when present in or spiked to a natural system. For distilled water the heat step is not necessary.

1.3 The range of the method may be varied through instrument and/or recorder expansion. Using a 100 ml sample, a detection limit of 0.2 μg Hg/l can be achieved; concentrations below this level should be reported as <0.2 (see Appendix 11.2).

2. Summary of Method

2.1 The flameless AA procedure is a physical method based on the absorption of radiation at 253.7 nm by mercury vapor. The mercury is reduced to the elemental state and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance (peak height) is measured as a function of mercury concentration and recorded in the usual manner.

3. Sample Handling and Preservation

3.1 Until more conclusive data are obtained, samples should be preserved by acidification with nitric acid to a pH of 2 or lower immediately at the time of collection. If only dissolved mercury is to be determined, the sample should be filtered through an all glass apparatus before the acid is added. For total mercury the filtration is omitted.

4. Interference

4.1 Possible interference from sulfide is eliminated by the addition of potassium permanganate. Concentrations as high as 20 mg/l of sulfide as sodium sulfide do not interfere with the recovery of added inorganic mercury from distilled water.

4.2 Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/l had no effect on recovery of mercury from spiked samples.

4.3 Sea waters, brines and industrial effluents high in chlorides require additional permanganate (as much as 25 ml). During the oxidation step, chlorides are converted to free chlorine which will also absorb radiation at 253 nm. Care must be taken to assure that free chlorine is absent before the mercury is reduced and swept into the cell. This may be accomplished by using an excess of hydroxylamine sulfate reagent (25 ml). In addition, the dead air space in the BOD bottle must be purged before the addition of stannous sulfate. Both inorganic and organic mercury spikes have been quantitatively recovered from sea water using this technique.

4.4 Interference from certain volatile organic materials which will absorb at this wavelength is also possible. A preliminary run without reagents should determine if this type of interference is present (see Appendix 11.1).

5. Apparatus

5.1 Atomic Absorption Spectrophotometer: (See Note 1) Any atomic absorption unit having an open sample presentation area in which to mount the absorption cell is suitable. Instrument settings recommended by the particular manufacturer should be followed. Note 1: Instruments designed specifically for the measurement of mercury using the cold vapor technique are commercially available and may be substituted for the atomic absorption spectrophotometer.

5.2 Mercury Hollow Cathode Lamp: Westinghouse WL-22847, argon filled, or equivalent.

5.3 Recorder: Any multi-range variable speed recorder that is compatible with the UV detection system is suitable.

5.4 Absorption Cell: Standard spectrophotometer cells 10 cm long, having quartz end windows may be used. Suitable cells may be constructed from plexiglass tubing, 1" O.D. X 4-1/2". The ends are ground perpendicular to the longitudinal axis and quartz windows (1" diameter X 1/16" thickness) are cemented in place. Gas inlet and outlet ports (also of plexiglass but 1/4" O.D.) are attached approximately

1/2″ from each end. The cell is strapped to a burner for support and aligned in the light beam by use of two 2″ by 2″ cards. One inch diameter holes are cut in the middle of each card; the cards are then placed over each end of the cell. The cell is then positioned and adjusted vertically and horizontally to give the maximum transmittance.

5.5 Air Pump: Any peristaltic pump capable of delivering 1 liter of air per minute may be used. A Masterflex pump with electronic speed control has been found to be satisfactory.

5.6 Flowmeter: Capable of measuring an air flow of 1 liter per minute.

5.7 Aeration Tubing: A straight glass frit having a coarse porosity. Tygon tubing is used for passage of the mercury vapor from the sample bottle to the absorption cell and return.

5.8 Drying Tube: 6″ X 3/4″ diameter tube containing 20 g of magnesium perchlorate (see Note 2). The apparatus is assembled as shown in Figure 1.

NOTE 2: In place of the magnesium perchlorate drying tube, a small reading lamp with 60W bulb may be used to prevent condensation of moisture inside the cell. The lamp is positioned to shine on the absorption cell maintaining the air temperature in the cell about 10°C above ambient.

6. Reagents

6.1 Sulfuric Acid, Conc: Reagent grade.

6.1.1 Sulfuric acid, 0.5 N: Dilute 14.0 ml of conc. sulfuric acid to 1.0 liter.

6.2 Nitric Acid, Conc: Reagent grade of low mercury content (See Note 3).

NOTE 3: If a high reagent blank is obtained, it may be necessary to distill the nitric acid.

6.3 Stannous Sulfate: Add 25 g stannous sulfate to 250 ml of 0.5 N sulfuric acid. This mixture is a suspension and should be stirred continuously during use. (Stannous chloride may be used in place of stannous sulfate.)

6.4 Sodium Chloride-Hydroxylamine Sulfate Solution: Dissolve 12 g of sodium chloride and 12 g of hydroxylamine sulfate in distilled water and dilute to 100.0 ml. (Hydroxylamine hydrochloride may be used in place of hydroxylamine sulfate.)

6.5 Potassium Permanganate: 5% solution, w/v. Dissolve 5 g of potassium permanganate in 100 ml of distilled water.

6.6 Potassium Persulfate: 5% solution, w/v. Dissolve 5 g of potassium persulfate in 100 ml of distilled water.

6.7 Stock Mercury Solution: Dissolve 0.1354 g of mercuric chloride in 75 ml of distilled water. Add 10 ml of conc. nitric acid and adjust the volume to 100.0 ml. 1 ml = 1 mg Hg.

6.8 Working Mercury Solution: Make successive dilutions of the stock mercury solution to obtain a working standard containing 0.1 μg per ml. This working standard and the dilutions of the stock mercury solution should be prepared fresh daily. Acidity of the working standard should be maintained at 0.15% nitric acid. This acid should be added to the flask as needed before the addition of the aliquot.

7. Calibration

7.1 Transfer 0, 0.5, 1.0, 2.0, 5.0 and 10.0 ml aliquots of the working mercury solution containing 0 to 1.0 μg of mercury to a series of 300 ml BOD bottles. Add enough distilled water to each bottle to make a total volume of 100 ml. Mix thoroughly and add 5 ml of conc. sulfuric acid (6.1) and 2.5 ml of conc. nitric acid (6.2) to each bottle. Add 15 ml of $KMnO_4$ (6.5) solution to each bottle and allow to stand at least 15 minutes. Add 8 ml of potassium persulfate (6.6) to each bottle and heat for 2 hours in a water bath maintained at 95°C. Cool and add 6 ml of sodium chloride-hydroxylamine sulfate solution (6.4) to reduce the excess permanganate. When the solution has been decolorized wait 30 seconds, add 5 ml of the stannous sulfate solution (6.3) and immediately attach the bottle to the aeration apparatus forming a closed system. At this point the sample is allowed to stand quietly without manual agitation. The circulating pump, which has previously been adjusted to a rate of 1 liter per minute, is allowed to run continuously (See Note 4). The absorbance will increase and reach maximum within 30 seconds. As soon as the recorder pen levels off, approximately 1 minute, open the bypass valve and continue the aeration until the absorbance returns to its minimum value (see Note 5). Close the bypass valve, remove the stopper and frit from the BOD bottle and continue the aeration. Proceed with the standards and construct a standard curve by plotting peak height versus micrograms of mercury.

NOTE 4: An open system where the mercury vapor is passed through the absorption cell only once may be used instead of the closed system.

NOTE 5: Because of the toxic nature of mercury vapor precaution must be taken to avoid its inhalation. Therefore, a bypass has been included in the system to either vent the mercury vapor into an exhaust hood or pass the vapor through some absorbing media, such as:

a) equal volumes of 0.1 M $KMnO_4$ and 10% H_2SO_4

b) 0.25% iodine in a 3% KI solution

A specially treated charcoal that will adsorb mercury vapor is also available from Barnebey and Cheney, E. 8th Ave. and N. Cassidy St., Columbus, Ohio 43219, Cat. #580-13 or #580-22.

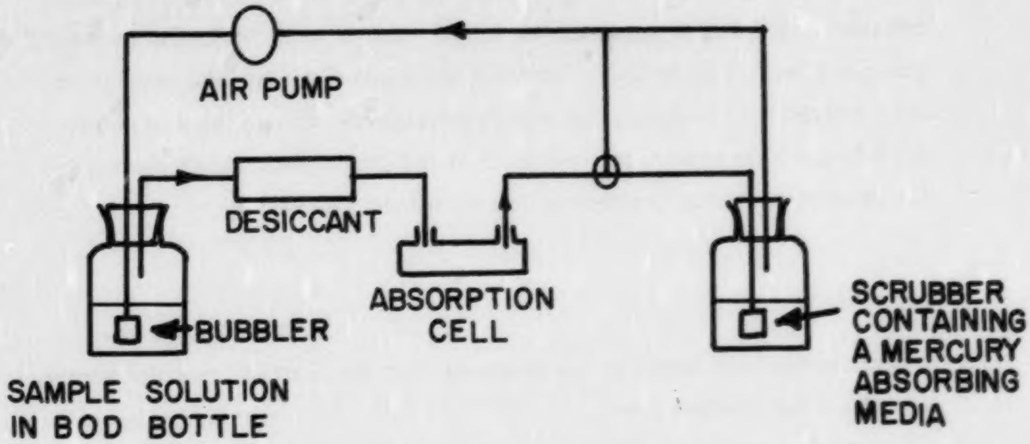

AIR PUMP
DESICCANT
ABSORPTION CELL
BUBBLER
SAMPLE SOLUTION IN BOD BOTTLE
SCRUBBER CONTAINING A MERCURY ABSORBING MEDIA

FIGURE 1. APPARATUS FOR FLAMELESS MERCURY DETERMINATION

8. Procedure

8.1 Transfer 100 ml or an aliquot diluted to 100 ml, containing not more than 1.0μg of mercury, to a 300 ml BOD bottle. Add 5 ml of sulfuric acid (6.1) and 2.5 ml of conc. nitric acid (6.2) mixing after each addition. Add 15 ml of potassium permanganate solution (6.5) to each sample bottle. For sewage samples additional permanganate may be required. Shake and add additional portions of potassium permanganate solution, if necessary, until the purple color persists for at least 15 minutes. Add 8 ml of potassium persulfate (6.6) to each bottle and heat for 2 hours in a water bath at 95°C. Cool and add 6 ml of sodium chloride-hydroxylamine sulfate (6.4) to reduce the excess permanganate. After a delay of at least 30 seconds add 5 ml of stannous sulfate (6.3) and immediately attach the bottle to the aeration apparatus. Continue as described under Calibration.

9. Calculation

9.1 Determine the peak height of the unknown from the chart and read the mercury value from the standard curve.

9.2 Calculate the mercury concentration in the sample by the formula:

$$\mu\text{gHg/l} = \left(\frac{\mu\text{g Hg in}}{\text{aliquot}}\right)\left(\frac{1000}{\text{vol. of aliquot in ml.}}\right)$$

9.3 Report mercury concentrations as follows: Below 0.2 μg/l, <0.2; between 1 and 10 μg/l, one decimal; above 10 μg/l, whole numbers.

10. Precision and Accuracy

10.1 In a single laboratory (MDQARL), using an Ohio River composite sample with a background mercury concentration of 0.35 μg/l, spiked with concentrations of 1, 3 and 4 μg/l, the standard deviations were ±0.14, ±0.10 and ±0.08, respectively. Standard deviation at the 0.35 level was ±0.16. Percent recoveries at the three levels were 89, 87, and 87%, respectively.

10.2 In a joint EPA/ASTM interlaboratory study of the cold vapor technique for total mercury in water, increments of organic and inorganic mercury were added to natural waters. Recoveries were determined by difference. A statistical summary of this study follows:

Number of Labs	True Values µg/liter	Mean Value µg/liter	Standard Deviation µg/liter	Accuracy as % Bias
76	0.21	0.349	0.276	66
80	0.27	0.414	0.279	53
82	0.51	0.674	0.541	32
77	0.60	0.709	0.390	18
82	3.4	3.41	1.49	0.34
79	4.1	3.81	1.12	−7.1
79	8.8	8.77	3.69	−0.4
78	9.6	9.10	3.57	−5.2

11. Appendix

11.1 While the possibility of absorption from certain organic substances actually being present in the sample does exist, the MDQAR Laboratory has not encountered such samples. This is mentioned only to caution the analyst of the possibility. A simple correction that may be used is as follows: If an interference has been found to be present (4.4), the sample should be analyzed both by using the regular procedure and again under oxidizing conditions only, that is without the reducing reagents. The true mercury value can then be obtained by subtracting the two values.

11.2 If additional sensitivity is required, a 200 ml sample with recorder expansion may be used provided the instrument does not produce undue noise. Using a Coleman MAS-50 with a drying tube of magnesium perchlorate and a variable recorder, 2 mv was set to read full scale. With these conditions, and distilled water solutions of mercuric chloride at concentrations of 0.15, 0.10, 0.05 and 0.025 µg/l the standard deviations were ±0.027, ±0.006, ±0.01 and ±0.004. Percent recoveries at these levels were 107, 83, 84 and 96%, respectively.

11.3 Directions for the disposal of mercury-containing wastes are given in ASTM Standards, Part 23, Water and Atmospheric Analysis, p 352, Method D3223 (1973).

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MERCURY IN WATER

(Automated Cold Vapor Technique)

STORET NO. 71900

1. Scope and Application

   1.1 This method is applicable to surface waters. It may be applicable to saline waters, wastewaters, effluents, and domestic sewages providing potential interferences are not present (See Interference 4).

   1.2 The working range is 0.2 to 20.0 μg Hg/l.

2. Summary of Method

   2.1 The flameless AA procedure is a physical method based on the absorption of radiation at 253.7 nm by mercury vapor. The mercury is reduced to the elemental state and aerated from solution. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance (peak height) is measured as a function of mercury concentration and recorded in the usual manner.

   2.2 In addition to inorganic forms of mercury, organic mercurials may also be present. These organo-mercury compounds will not respond to the flameless atomic absorption technique unless they are first broken down and converted to mercuric ions. Potassium permanganate oxidizes many of these compounds but recent studies have shown that a number of organic mercurials, including phenyl mercuric acetate and methyl mercuric chloride, are only partially oxidized by this reagent. Potassium persulfate has been found to give approximately 100% recovery when used as the oxidant with these compounds. Therefore, an automated persulfate oxidation step following the automated addition of the permanganate has been included to insure that organo-mercury compounds, if present, will be oxidized to the mercuric ion before measurement.

3. Sample Handling and Preservation

   3.1 Until more conclusive data are obtained, samples should be preserved by acidification with nitric acid to a pH of 2 or lower immediately at the time of collection.(1) If only dissolved mercury is to be determined, the sample should be filtered before the acid is added. For total mercury the filtration is omitted.

4. Interference (See NOTE 1)

   4.1 Some sea waters and wastewaters high in chlorides have shown a positive interference, probably due to the formation of free chlorine.

4.2 Interference from certain volatile organic materials which will absorb at this wavelength is also possible. A preliminary run under oxidizing conditions, without stannous sulfate, would determine if this type of interference is present.

4.3 Formation of a heavy precipitate, in some wastewaters and effluents, has been reported upon addition of concentrated sulfuric acid. If this is encountered, the problem sample cannot be analyzed by this method.

4.4 Samples containing solids must be blended and then mixed while being sampled if total mercury values are to be reported.

NOTE 1: All the above interferences can be overcome by use of the Manual Mercury method in this manual.

5. Apparatus

5.1 Technicon AutoAnalyzer consisting of:

5.1.1 Sampler II with provision for sample mixing.

5.1.2 Manifold.

5.1.3 Proportioning Pump II or III.

5.1.4 High temperature heating bath with two distillation coils (Technicon Part #116-0163) in series.

5.2 Vapor-liquid separator (Figure 1).

5.3 Absorption cell, 100 mm long, 10 mm diameter with quartz windows.

5.4 Atomic Absorption Spectrophotometer (See Note 2): Any atomic absorption unit having an open sample presentation area in which to mount the absorption cell is suitable. Instrument settings recommended by the particular manufacturer should be followed.

NOTE 2: Instruments designed specifically for the measurement of mercury using the cold vapor technique are commercially available and may be substituted for the atomic absorption spectrophotometer.

5.5 Mercury Hollow Cathode Lamp: Westinghouse WL-22847, argon filled, or equivalent.

5.6 Recorder: Any multi-range variable speed recorder that is compatible with the UV detection system is suitable.

5.7 Source of cooling water for jacketed mixing coil and connector A-7.

5.8 Heat lamp: A small reading lamp with 60W bulb may be used to prevent condensation of moisture inside the cell. The lamp is positioned to shine on the absorption cell maintaining the air temperature in the cell about 10°C above ambient.

6. Reagents

6.1 Sulfuric Acid, Conc: Reagent grade

6.1.1 Sulfuric acid, 2 N: Dilute 56 ml of conc. sulfuric acid to 1 liter with distilled water.

6.1.2 Sulfuric acid, 10%: Dilute 100 ml conc. sulfuric acid to 1 liter with distilled water.

6.2 Nitric acid, Conc: Reagent grade of low mercury content.

6.2.1 Nitric Acid, 0.5% Wash Solution: Dilute 5 ml of conc. nitric acid to 1 liter with distilled water.

6.3 Stannous Sulfate: Add 50 g stannous sulfate to 500 ml of 2 N sulfuric acid (6.1.1). This mixture is a suspension and should be stirred continuously during use.

NOTE 3: Stannous chloride may be used in place of stannous sulfate.

6.4 Sodium Chloride-Hydroxylamine Sulfate Solution: Dissolve 30 g of sodium chloride and 30 g of hydroxylamine sulfate in distilled water to 1 liter.

NOTE 4: Hydroxylamine hydrochloride may be used in place of hydroxylamine sulfate.

6.5 Potassium Permanganate: 0.5% solution, w/v. Dissolve 5 g of potassium permanganate in 1 liter of distilled water.

6.6 Potassium Permanganate, 0.1 N: Dissolve 3.16 g of potassium permanganate in distilled water and dilute to 1 liter.

6.7 Potassium Persulfate: 0.5% solution, w/v. Dissolve 5 g of potassium persulfate in 1 liter of distilled water.

6.8 Stock Mercury Solution: Dissolve 0.1354 g of mercuric chloride in 75 ml of distilled water. Add 10 ml of conc. nitric acid and adjust the volume to 100.0 ml. 1.0 ml = 1.0 mg Hg.

6.9 Working Mercury Solution: Make successive dilutions of the stock mercury solution (6.8) to obtain a working standard containing 0.1 μg per ml. This working standard and the dilutions of the stock mercury solution should be prepared fresh daily. Acidity of the working standard should be maintained at 0.15% nitric acid. This acid should be added to the flask as needed before the addition of the aliquot. From this solution prepare standards containing 0.2, 0.5, 1.0, 2.0, 5.0, 10.0, 15.0 and 20.0 μg Hg/l.

6.10 Air Scrubber Solution: Mix equal volumes of 0.1 N potassium permanganate (6.6) and 10% sulfuric acid (6.1.2).

7. Procedure

7.1 Set up manifold as shown in Figure 2.

7.2 Feeding all the reagents through the system with acid wash solution (6.2.1) through the sample line, adjust heating bath to 105°C.

7.3 Turn on atomic absorption spectrophotometer, adjust instrument settings as recommended by the manufacturer, align absorption cell in light path for maximum transmittance and place heat lamp directly over absorption cell.

7.4 Arrange working mercury standards from 0.2 to 20.0 μg Hg/l in sampler and start sampling. Complete loading of sample tray with unknown samples.

7.5 Prepare standard curve by plotting peak height of processed standards against concentration values. Determine concentration of samples by comparing sample peak height with standard curve.

NOTE 5: Because of the toxic nature of mercury vapor, precaution must be taken to avoid its inhalation. Venting the mercury vapor into an exhaust hood or passing the vapor through some absorbing media such as:

a) equal volumes of 0.1 N $KMnO_4$ (6.6) and 10% H_2SO_4 (6.1.2).

b) 0.25% iodine in a 3% KI solution, is recommended.

A specially treated charcoal that will adsorb mercury vapor is also available from Barnebey and Cheney, E. 8th Ave. and North Cassidy St., Columbus, Ohio 43219, Cat. #580-13 or #580-22.

7.6 After the analysis is complete put all lines except the H_2SO_4 line in distilled water to wash out system. After flushing, wash out the H_2SO_4 line. Also flush the coils in the high temperature heating bath by pumping stannous sulfate (6.3) through the sample lines followed by distilled water. This will prevent build-up of oxides of manganese.

8. Precision and Accuracy

8.1 In a single laboratory (SEWL), using distilled water standards at concentrations of 0.5, 1.0, 2.0, 5.0, 10.0 and 20.0 μg Hg/l, the standard deviations were ±0.04, ±0.07, ±0.09, ±0.20, ±0.40 and ±0.84 μg/l, respectively.

8.2 In a single laboratory (SEWL), using surface water samples spiked with ten organic mercurials at the 10 μg/l level, recoveries ranged from 87 to 117%. Recoveries of the same ten organic mercurials in distilled water at the 10 μg/l level, ranged from 92 to 125%.

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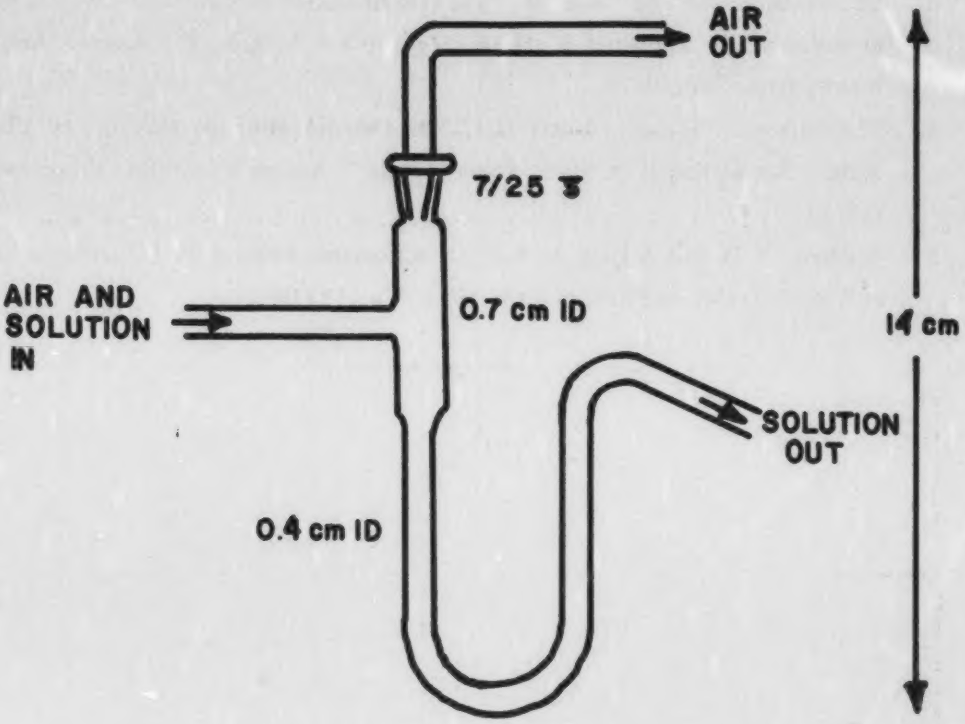
AIR
OUT
7/25 ₸
AIR AND
SOLUTION
IN
0.7 cm ID
14 cm
SOLUTION
OUT
0.4 cm ID

FIGURE 1. VAPOR LIQUID SEPARATOR

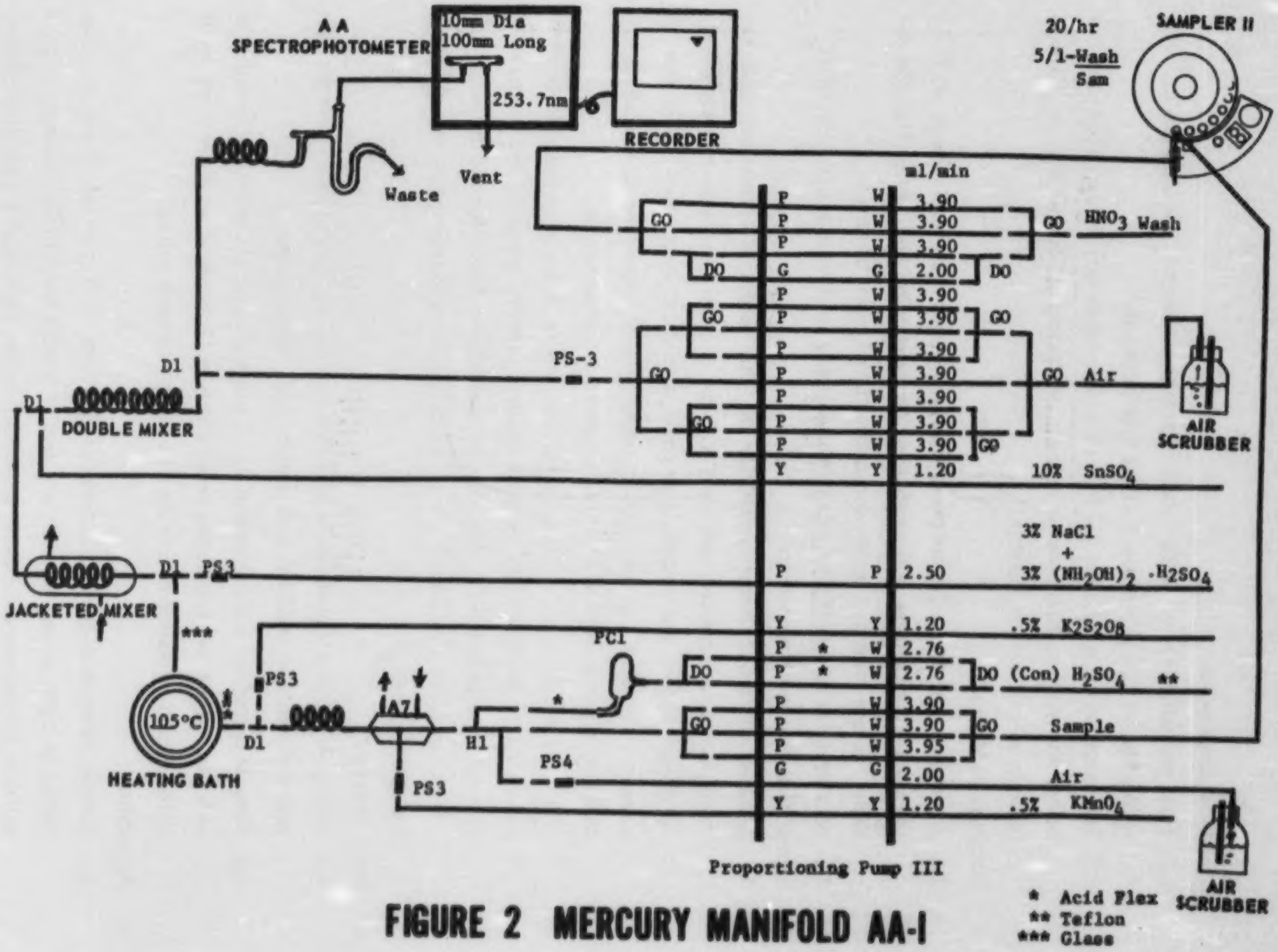
A A SPECTROPHOTOMETER
10mm Dia
100mm Long
253.7nm
Vent
Waste
RECORDER
20/hr
5/1-Wash/Sam
SAMPLER II
ml/min
P W 3.90
P W 3.90
P W 3.90
G G 2.00
P W 3.90
P W 3.90
P W 3.90
P W 3.90
P W 3.90
P W 3.90
P W 3.90
Y Y 1.20
P P 2.50
Y Y 1.20
P * W 2.76
P * W 2.76
P W 3.90
P W 3.90
P W 3.95
G G 2.00
Y Y 1.20
GO
DO
HNO3 Wash
Air
AIR SCRUBBER
10% SnSO4
3% NaCl + 3% (NH2OH)2 .H2SO4
.5% K2S2O8
(Con) H2SO4 **
Sample
Air
.5% KMnO4
D1
PS-3
DOUBLE MIXER
D1 PS3
JACKETED MIXER
***
PS3
105°C
HEATING BATH
D1
A7
PS3
H1
PS4
PC1
*
Proportioning Pump III
* Acid Flex
** Teflon
*** Glass

FIGURE 2 MERCURY MANIFOLD AA-I

MERCURY IN SEDIMENT

(Manual Cold Vapor Technique)

1. Scope and Application

   1.1 This procedure(1) measures total mercury (organic + inorganic) in soils, sediments, bottom deposits and sludge type materials.

   1.2 The range of the method is 0.2 to 5 μg/g. The range may be extended above or below the normal range by increasing or decreasing sample size or through instrument and recorder control.

2. Summary of Method

   2.1 A weighed portion of the sample is digested in aqua regia for 2 minutes at 95°C, followed by oxidation with potassium permanganate. Mercury in the digested sample is then measured by the conventional cold vapor technique.

   2.2 An alternate digestion(2) involving the use of an autoclave is described in (8.2).

3. Sample Handling and Preservation

   3.1 Because of the extreme sensitivity of the analytical procedure and the omnipresence of mercury, care must be taken to avoid extraneous contamination. Sampling devices and sample containers should be ascertained to be free of mercury; the sample should not be exposed to any condition in the laboratory that may result in contact or air-borne mercury contamination.

   3.2 While the sample may be analyzed without drying, it has been found to be more convenient to analyze a dry sample. Moisture may be driven off in a drying oven at a temperature of 60°C. No mercury losses have been observed by using this drying step. The dry sample should be pulverized and thoroughly mixed before the aliquot is weighed.

4. Interferences

   4.1 The same types of interferences that may occur in water samples are also possible with sediments, ie., sulfides, high copper, high chlorides, etc.

   4.2 Volatile materials which absorb at 253.7 nm will cause a positive interference. In order to remove any interfering volatile materials, the dead air space in the BOD bottle should be purged before the addition of stannous sulfate.

5. Apparatus

   5.1 Atomic Absorption Spectrophotometer (See Note 1): Any atomic absorption unit having an open sample presentation area in which to mount the absorption cell is suitable. Instrument settings recommended by the particular manufacturer should be followed.

NOTE 1: Instruments designed specifically for the measurement of mercury using the cold vapor technique are commercially available and may be substituted for the atomic absorption spectrophotometer.

5.2 Mercury Hollow Cathode Lamp: Westinghouse WL-22847, argon filled, or equivalent.

5.3 Recorder: Any multi-range variable speed recorder that is compatible with the UV detection system is suitable.

5.4 Absorption Cell: Standard spectrophotometer cells 10 cm long, having quartz end windows may be used. Suitable cells may be constructed from plexiglass tubing, 1" O.D. × 4-1/2". The ends are ground perpendicular to the longitudinal axis and quartz windows (1" diameter × 1/16" thickness) are cemented in place. Gas inlet and outlet ports (also of plexiglass but 1/4" O.D.) are attached approximately 1/2" from each end. The cell is strapped to a burner for support and aligned in the light beam to give the maximum transmittance.

NOTE 2: Two 2" × 2" cards with one inch diameter holes may be placed over each end of the cell to assist in positioning the cell for maximum transmittance.

5.5 Air Pump: Any peristaltic pump capable of delivering 1 liter of air per minute may be used. A Masterflex pump with electronic speed control has been found to be satisfactory. (Regulated compressed air can be used in an open one-pass system.)

5.6 Flowmeter: Capable of measuring an air flow of 1 liter per minute.

5.7 Aeration Tubing: Tygon tubing is used for passage of the mercury vapor from the sample bottle to the absorption cell and return. Straight glass tubing terminating in a coarse porous frit is used for sparging air into the sample.

5.8 Drying Tube: 6" × 3/4" diameter tube containing 20 g of magnesium perchlorate (See Note 3). The apparatus is assembled as shown in the accompanying diagram.

NOTE 3: In place of the magnesium perchlorate drying tube, a small reading lamp with 60W bulb may be used to prevent condensation of moisture inside the cell. The lamp is positioned to shine on the absorption cell maintaining the air temperature in the cell about 10°C above ambient.

6. Reagents

6.1 Aqua Regia: Prepare immediately before use by carefully adding three volumes of conc. HCl to one volume of conc. HNO_3.

6.2 Sulfuric Acid, 0.5 N: Dilute 14.0 ml of conc. sulfuric acid to 1 liter.

6.3 Stannous Sulfate: Add 25 g stannous sulfate to 250 ml of 0.5 N sulfuric acid (6.2). This mixture is a suspension and should be stirred continuously during use.

6.4 Sodium Chloride-Hydroxylamine Sulfate Solution: Dissolve 12 g of sodium chloride and 12 g of hydroxylamine sulfate in distilled water and dilute to 100 ml.

NOTE 4: A 10% solution of stannous chloride may be substituted for (6.3) and hydroxylamine hydrochloride may be used in place of hydroxylamine sulfate in (6.4).

6.5 Potassium Permanganate: 5% solution, w/v. Dissolve 5 g of potassium permanganate in 100 ml of distilled water.

6.6 Stock Mercury Solution: Dissolve 0.1354 g of mercuric chloride in 75 ml of distilled water. Add 10 ml of conc. nitric acid and adjust the volume to 100.0 ml. 1.0 ml = 1.0 mg Hg.

6.7 Working Mercury Solution: Make successive dilutions of the stock mercury solution (6.6) to obtain a working standard containing 0.1 μg/ml. This working standard and the dilution of the stock mercury solutions should be prepared fresh daily. Acidity of the working standard should be maintained at 0.15% nitric acid. This acid should be added to the flask as needed before the addition of the aliquot.

7. Calibration

7.1 Transfer 0, 0.5, 1.0, 2.0, 5.0 and 10 ml aliquots of the working mercury solution (6.7) containing 0 to 1.0 μg of mercury to a series of 300 ml BOD bottles. Add enough distilled water to each bottle to make a total volume of 10 ml. Add 5 ml of aqua regia (6.1) and heat 2 minutes in a water bath at 95°C. Allow the sample to cool and add 50 ml distilled water and 15 ml of $KMnO_4$ solution (6.5) to each bottle and return to the water bath for 30 minutes. Cool and add 6 ml of sodium chloride-hydroxylamine sulfate solution (6.4) to reduce the excess permanganate. Add 50 ml of distilled water. Treating each bottle individually, add 5 ml of stannous sulfate solution (6.3) and immediately attach the bottle to the aeration apparatus. At this point, the sample is allowed to stand quietly without manual agitation. The circulating pump, which has previously been adjusted to a rate of 1 liter per minute, is allowed to run continuously. The absorbance, as exhibited either on the spectrophotometer or the recorder, will increase and reach maximum within 30 seconds. As soon as the recorder pen levels off, approximately 1 minute, open the bypass valve and continue the aeration until the absorbance returns to its minimum value (See Note 5). Close the bypass valve, remove the fritted tubing from the BOD bottle and continue the aeration. Proceed with the standards and construct a standard curve by plotting peak height versus micrograms of mercury.

NOTE 5: Because of the toxic nature of mercury vapor precaution must be taken to avoid its inhalation. Therefore, a bypass has been included in the system to either vent the mercury vapor into an exhaust hood or pass the vapor through some absorbing media, such as:

a) equal volumes of 0.1 N $KMnO_4$ and 10% H_2SO_4

b) 0.25% iodine in a 3% KI solution.

A specially treated charcoal that will absorb mercury vapor is also available from Barnebey and Cheney, E. 8th Ave. and North Cassidy St., Columbus, Ohio 43219, Cat. #580-13 or #580-22.

8. Procedure

8.1 Weigh triplicate 0.2 g portions of dry sample and place in bottom of a BOD bottle. Add 5 ml of distilled water and 5 ml of aqua regia (6.1). Heat 2 minutes in a water bath at 95°C. Cool, add 50 ml distilled water and 15 ml potassium permanganate solution (6.5) to each sample bottle. Mix thoroughly and place in the water bath for 30 minutes at 95°C. Cool and add 6 ml of sodium chloride-hydroxylamine sulfate (6.4) to reduce the excess permanganate. Add 55 ml of distilled water. Treating each bottle individually, add 5 ml of stannous sulfate (6.3) and immediately attach the bottle to the aeration apparatus. Continue as described under (7.1).

8.2 An alternate digestion procedure employing an autoclave may also be used. In this method 5 ml of conc. H_2SO_4 and 2 ml of conc. HNO_3 are added to the 0.2 g of sample. 5 ml of saturated $KMnO_4$ solution is added and the bottle covered with a piece of aluminum foil. The samples are autoclaved at 121°C and 15 lbs. for 15 minutes. Cool, make up to a volume of 100 ml with distilled water and add 6 ml of sodium chloride-hydroxylamine sulfate solution (6.4) to reduce the excess permanganate. Purge the dead air space and continue as described under (7.1).

9. Calculation

9.1 Measure the peak height of the unknown from the chart and read the mercury value from the standard curve.

9.2 Calculate the mercury concentration in the sample by the formula:

$$\mu g\ Hg/g = \frac{\mu g\ Hg \text{ in the aliquot}}{\text{wt of the aliquot in gms.}}$$

9.3 Report mercury concentrations as follows: Below 0.1 µg/gm, <0.1; between 0.1 and 1 µg/gm, to the nearest 0.01 µg; between 1 and 10 µg/gm, to nearest 0.1 µg; above 10 µg/gm, to nearest µg.

10. Precision and Accuracy

10.1 The following standard deviations on replicate sediment samples were recorded at the indicated levels; 0.29 μg/g ±0.02 and 0.82 μg/g ±0.03. Recovery of mercury at these levels, added as methyl mercuric chloride, was 97 and 94%, respectively.

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MOLYBDENUM

(Standard Conditions)

STORET NO. Total 01062

Optimum Concentration Range: 0.5-20 mg/l using a wavelength of 313.3 nm

Sensitivity: 0.3 mg/l

Detection Limit: 0.1 mg/l

Preparation of Standard Solution

1. Stock Solution: Dissolve 1.840 g of ammonium molybdate $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ (analytical reagent grade) in deionized distilled water and dilute to 1 liter. 1 ml = 1 mg Mo (1000 mg/l).
2. Aluminum nitrate solution: Dissolve 139 g aluminum nitrate, $Al(NO_3)_3 \cdot 9H_2O$, in 150 ml of deionized distilled water; heat to effect solution. Allow to cool and make up to 200 ml.
3. Prepare dilutions of the stock molybdenum solution to be used as calibration standards at the time of analysis. To each 100 ml of standard and sample alike, add 2 ml of the aluminum nitrate solution. The *calibration standards* should be prepared using the same type of acid (HCl or HNO_3) and at the same concentration as the samples for analysis.

Sample Preparation

1. The procedure for the determination of total metals as given in part 4.1.3 of the Atomic Absorption Methods section of this manual has been found to be satisfactory.

Instrumental Parameters (General)

1. Molybdenum hollow cathode lamp
2. Wavelength: 313.3 nm
3. Fuel: Acetylene
4. Oxidant: Nitrous Oxide
5. Type of flame: Fuel rich

Interferences

1. With the recommended nitrous oxide-acetylene flame, interferences of calcium and other ions may be controlled by adding 1000 mg/l of a refractory metal such as aluminum [Anal. Chem. Acta *44*, 437 (1969)]. This should be done to both samples and standards alike.

Notes

1. For low levels of molybdenum an oxine extraction procedure may be useful. (Ref: Chau et.al., Anal. Chem. Acta *48*, 205, 1969).
2. Data to be entered into STORET must be reported as μg/l.

Precision and Accuracy

1. In a single laboratory (MDQARL), using a mixed industrial-domestic waste effluent at concentrations of 0.30, 1.5 and 7.5 mg Mo/l, the standard deviations were ±0.007, ±0.02 and ±0.07, respectively. Recoveries at these levels were 100%, 96% and 95%, respectively.

NICKEL

(Standard Conditions)

STORET NO. Total 01067

Optimum Concentration Range: 0.3-10 mg/l using a wavelength of 232.0 nm

Sensitivity: 0.15 mg/l

Detection List: 0.02 mg/l

Preparation of Standard Solution

1. Stock Solution: Dissolve 4.953 g of nickel nitrate, $Ni(NO_3)_2 \cdot 6H_2O$ (analytical reagent grade) in deionized distilled water. Add 10 ml of conc. nitric acid and dilute to 1 liter with deionized distilled water. 1 ml = 1 mg Ni (1000 mg/l).
2. Prepare dilutions of the stock nickel solution to be used as calibration standards at the time of analysis. The *calibration standards* should be prepared using the same type of acid (HCl or HNO_3) and at the same concentration as the samples for analysis.

Sample Preparation

1. The procedure for the determination of total metals as given in part 4.1.3 of the Atomic Absorption Methods section of this manual has been found to be satisfactory.

Instrumental Parameters (General)

1. Nickel hollow cathode lamp
2. Wavelength: 232.0 nm
3. Fuel: Acetylene
4. Oxidant: Air
5. Type of Flame: Oxidizing

Interferences

1. The 352.4 nm wavelength is less susceptible to nonatomic absorbance and may be used. The calibration curve is more linear at this wavelength; however, there is some loss of sensitivity.

Notes

1. For levels of nickel below 50 μg/l, the extraction procedure is recommended.
2. Data to be entered into STORET must be reported as μg/l.
3. The heptoxime method may be used (Standard Methods, 13th Edition, p 443).

Precision and Accuracy

1. In a single laboratory (MDQARL), using a mixed industrial-domestic waste effluent at concentrations of 0.20, 1.0 and 5.0 mg Ni/l, the standard deviations were ±0.011, ±0.02 and ±0.04, respectively. Recoveries at these levels were 100%, 97% and 93%, respectively.

POTASSIUM

(Standard Conditions)

STORET NO. Total 00937

Optimum Concentration Range: 0.1-2 mg/l using a wavelength of 766.5 nm

Sensitivity: 0.04 mg/l

Detection Limit: 0.005 mg/l

Preparation of Standard Solution

1. Stock Solution: Dissolve 0.1907 g of KCl (analytical reagent grade), dried at 110°C, in deionized distilled water and make up to 1 liter. 1 ml = 0.10 mg K (100 mg/1).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis.

Sample Preparation

1. For the analysis of total postassium in domestic and industrial effluents, the procedure for the determination of total metals as given in part 4.1.3 of the Atomic Absorption Methods section of this manual has been found to be satisfactory.
2. For ambient waters, a representative aliquot of a well-mixed sample may also be used directly for analysis. If suspended solids are present in sufficient amounts to clog the nebulizer, the sample may be allowed to settle and the supernatant liquid analyzed directly.
3. Samples should be preserved with (1:1) nitric acid to a pH of 2 at the time of collection.

Instrumental Parameters (General)

1. Potassium hollow cathode lamp
2. Wavelength: 766.5 nm
3. Fuel: Acetylene
4. Oxidant: Air
5. Type of flame: Slightly oxidizing

Notes

1. The Osram potassium vapor-discharge lamp may also be used in the Perkin-Elmer 303. In this case the current should be 350 ma or the optimum operating current.
2. Sodium may interfere if present at much higher levels than the potassium. This effect can be compensated by approximately matching the sodium content of the potassium standards with that of the sample.

3. Potassium absorption is enhanced in the presence of Na, Li and Cs, especially in a high-temperature flame. This enhancement effect of sodium can be eliminated by changing the burner height and the type of flame used. The burner assembly is set approximately 0.05 cm below the optical light path so that the optical light path is sliced at the bottom by the burner head. A fuel-rich flame is used.
4. The 404.4 nm line may also be used. This line has a sensitivity of 5 mg/l for 1% absorption.
5. To cover the range of potassium values normally observed in surface waters (0.1-20 mg/l), it is suggested that the burner be rotated 75°.
6. The flame photometric or colorimetric methods may be used (Standard Methods, 13th Edition, p 283 & 285).
7. Data to be entered into STORET must be reported as mg/l.

Precision and Accuracy

1. In a single laboratory (MDQARL), using distilled water samples at concentrations of 1.6 and 6.3 mg/l, the standard deviations were ±0.2 and ±0.5, respectively. Recoveries at these levels were 103% and 102%.

SELENIUM

(Gaseous Hydride Method)

STORET NO. Total 01147

1. Scope and Application

   1.1 The gaseous hydride method determines inorganic selenium when present in concentrations at or above 2 μg/l. The method is applicable to most fresh and saline waters, in the absence of high concentrations of chromium, cobalt, copper, mercury, molybdenum, nickel and silver.

2. Summary of Method

   2.1 Selenium in the sample is reduced from the +6 oxidation state to the +4 oxidation state by the addition of $SnCl_2$. Zinc is added to the acidified sample, producing hydrogen and converting the selenium to the hydride, SeH_2. The gaseous selenium hydride is swept into an argon-hydrogen flame of an atomic absorption spectrophotometer. The working range of the method is 2-20 μg/l using the 196.0 nm wavelength.

3. Comments

   3.1 In analyzing most surface and ground waters, interferences are rarely encountered. Industrial waste samples should be spiked with a known amount of selenium to establish adequate recovery.

   3.2 Organic forms of selenium must be converted to an inorganic form and organic matter must be oxidized before beginning the analysis.

   3.3 Data to be entered into STORET must be reported as μg/l.

4. Precision and Accuracy

   4.1 Ten replicate solutions of selenium oxide at the 5, 10 and 15 μg/l level were analyzed by a single laboratory (Caldwell, Et.Al.). Standard deviations at these levels were ±0.6, ±1.1 and ±2.9 with recoveries of 100, 100 and 101%.

Bibliography

1. Caldwell, J. S., Lishka, R. J., and McFarren, E. F., "Evaluation of a Low-Cost Arsenic and Selenium Determination at Microgram per Liter Levels", JAWWA, vol 65, p. 731, Nov. 1973.

SILVER

(Standard Conditions)

STORET NO. Total 01077

Optimum Concentration Range: 0.1-4 mg/l using a wavelength of 328.1 nm

Sensitivity: 0.06 mg/l

Detection Limit: 0.01 mg/l

Preparation of Standard Solution

1. Stock Solution: Dissolve 1.575 g of $AgNO_3$ (analytical reagent grade) in deionized distilled water, add 10 ml conc. HNO_3 and make up to 1 liter. 1 ml = 1 mg Ag (1000 mg/l).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. Maintain an acid strength of 0.15% HNO_3 in all calibration standards.

Sample Preparation

1. The procedure for the determination of total metals as given in part 4.1.3 of the Atomic Absorption Methods section of this manual has been found to be satisfactory; however, the residue must be taken up in dilute nitric acid rather than hydrochloric to prevent precipitation of AgCl.

Instrumental Parameters (General)

1. Silver hollow cathode lamp
2. Wavelength: 328.1 nm
3. Fuel: Acetylene
4. Oxidant: Air
5. Type of flame: Oxidizing

Notes

1. For levels of silver below 20 $\mu g/1$, the extraction procedure is recommended.
2. Silver nitrate standards are light sensitive. Dilutions of the stock should be discarded after use as concentrations below 10 mg/l are not stable over long periods of time.
3. The 338.2 nm wavelength may also be used. This has a relative sensitivity of 3.
4. Data to be entered into STORET must be reported as $\mu g/l$.
5. The dithizone colorimetric method may be used (Standard Methods, 13th Edition, p 310).

SODIUM

(Standard Conditions)

STORET NO. Total 00929

Optimum Concentration Range: 0.03-1.0 mg/l using a wavelength of 589.6 nm

Sensitivity: 0.015 mg/l

Detection Limit: 0.002 mg/l

Preparation of Standard Solutions

1. Stock Solution: Dissolve 2.542 g of NaCl (analytical reagent grade), dried at 140°C, in deionized distilled water and make up to 1 liter. 1 ml = 1 mg Na (1000 mg/l).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis.

Sample Preparation

1. For the analysis of total sodium in domestic and industrial effluents, the procedure for the determination of total metals as given in part 4.1.3 of the Atomic Absorption Methods section of this manual has been found to be satisfactory.
2. For ambient waters, a representative aliquot of a well-mixed sample may be used directly for analysis. If suspended solids are present in sufficient amounts to clog the nebulizer, the sample may be allowed to settle and the supernatant liquid analyzed directly.
3. Samples should be preserved with (1:1) nitric acid to a pH of 2 at the time of collection.

Instrumental Parameters (General)

1. Sodium hollow cathode lamp
2. Wavelength: 589.6 nm
3. Fuel: Acetylene
4. Oxidant: Air
5. Type of flame: Oxidizing

Notes

1. The 330.2 nm resonance line of sodium yields a sensitivity of about 3 mg/l sodium for 1% absorption and provides a convenient way to avoid the need to dilute more concentrated solutions of sodium.

2. Low-temperature flames increase sensitivity by reducing the extent of ionization of this easily ionized metal. Ionization may also be controlled by adding potassium (1000 mg/l) to both standards and samples.
3. Data to be entered into STORET must be reported as mg/l.
4. The flame photometric method may be used (Standard Methods, 13th Edition, p 317).

Precision and Accuracy

1. In a single laboratory (MDQARL), using distilled water samples at levels of 8.2 and 52 mg/l, the standard deviations were ±0.1 and ±0.8, respectively. Recoveries at these levels were 102% and 100%.

THALLIUM

(Standard Conditions)

STORET NO. Total 01059

Optimum Concentration Range: 1-20 mg/l using a wavelength of 276.8 nm

Sensitivity: 0.5 mg/l

Detection Limit: 0.1 mg/l

Preparation of Standard Solution

1. Stock Solution: Dissolve 1.303 g of thallium nitrate, $TlNO_3$ (analytical reagent grade) in deionized distilled water. Add 10 ml of conc. nitric acid and dilute to 1 liter with deionized distilled water. 1 ml = 1 mg Tl (1000 mg/l).
2. Prepare dilutions of the stock thallium solution to be used as calibration standards at the time of analysis. The *calibration standards* should be prepared using the same type of acid (HCl or HNO_3) and at the same concentration as the samples for analysis.

Sample Preparation

1. The procedure for the determination of total metals as given in part 4.1.3 of the Atomic Absorption Methods section of this manual has been found to be satisfactory.

Instrumental Parameters (General)

1. Thallium hollow cathode lamp
2. Wavelength: 276.8 nm
3. Fuel: Acetylene
4. Oxidant: Air
5. Type of flame: Oxidizing

Notes

1. Data to be entered into STORET must be reported as μg/l.

Precision and Accuracy

1. In a single laboratory (MDQARL), using a mixed industrial-domestic waste effluent at concentrations of 0.60, 3.0 and 15 mg Tl/l, the standard deviations were ±0.018, ±0.05 and ±0.2, respectively. Recoveries at these levels were 100%, 98% and 98%, respectively.

TIN

(Standard Conditions)

STORET NO. Total 01102

Optimum Concentration Range: 10-200 mg/l using a wavelength of 286.3 nm

Sensitivity: 4 mg/l

Detection Limit: 0.8 mg/l

Preparation of Standard Solution

1. Stock Solution: Dissolve 1.000 g of tin metal (analytical reagent grade) in 100 ml of conc. HCl and dilute to 1 liter with deionized distilled water. 1 ml = 1 mg Sn (1000 mg/l).
2. Prepare dilutions of the stock tin solution to be used as calibration standards at the time of analysis. Maintain an acid concentration of 10% HCl in all solutions.

Sample Preparation

1. The procedure for the determination of total metals as given in part 4.1.3 of the Atomic Absorption Methods section of this manual has been found to be satisfactory.

Instrumental Parameters (General)

1. Tin hollow cathode lamp
2. Wavelength: 286.3 nm
3. Fuel: Acetylene
4. Oxidant: Air
5. Type of flame: Fuel rich

Notes

1. Data to be entered into STORET must be reported as μg/l.

Precision and Accuracy

1. In a single laboratory (MDQARL), using a mixed industrial-domestic waste effluent at concentrations of 4.0, 20 and 60 mg Sn/l, the standard deviations were ±0.25, ±0.5 and ±0.5, respectively. Recoveries at these levels were 96%, 101% and 101%, respectively.

TITANIUM

(Standard Conditions)

STORET NO. Total 01152

Optimum Concentration Range: 5-100 mg/l using a wavelength of 365.3 nm

Sensitivity: 2.0 mg/l

Detection Limit: 0.3 mg/l

Preparation of Standard Solution

1. Stock Solution: Dissolve 4.008 g of titanium sulfate, $Ti_2(SO_4)_3$, in dilute HCl and make up to 1 liter with deionized distilled water. 1 ml = 1 mg Ti (1000 mg/l).
2. Potassium chloride solution: Dissolve 95 g potassium chloride, KCl, in distilled water and make up to 1 liter.
3. Prepare dilutions of the stock titanium solution to be used as calibration standards at the time of analysis. To each 100 ml of standard and sample alike, add 2 ml of potassium chloride solution.

Sample Preparation

1. The procedure for the determination of total metals as given in part 4.1.3 of the Atomic Absorption Methods section of this manual must be modified by the addition of 3 ml of conc. sulfuric acid in addition to the nitric acid. This is necessary to keep any titanium that may be present in solution.

Instrumental Parameters (General)

1. Titanium hollow cathode lamp
2. Wavelength: 365.3 nm
3. Fuel: Acetylene
4. Oxidant: Nitrous Oxide
5. Type of flame: Fuel rich

Interferences

1. A number of elements increase the sensitivity of titanium. To control this problem, potassium (1000 mg/l) must be added to standards and samples alike. [Atomic Absorption Newsletter 6, p 86 (1967)]

Notes

1. Data to be entered into STORET must be reported as µg/l.

Precision and Accuracy

1. In a single laboratory (MDQARL), using a mixed industrial-domestic waste effluent at concentrations of 2.0, 10 and 50 mg Ti/l, the standard deviations were ±0.07, ±0.1 and ±0.4, respectively. Recoveries at these levels were 97%, 91% and 88%, respectively.

VANADIUM

(Standard Conditions)

STORET NO. Total 01087

Optimum Concentration Range: 1-100 mg/l using a wavelength of 318.4 nm

Sensitivity: 0.8 mg/l

Detection Limit: 0.2 mg/l

Preparation of Standard Solution

1. Stock Solution: Dissolve 1.7854 g of vanadium pentoxide, V_2O_5 (analytical reagent) in 10 ml of conc. nitric acid and dilute to 1 liter with deionized distilled water. 1 ml = 1 mg V (1000 mg/l).
2. Aluminum nitrate solution: Dissolve 139 g aluminum nitrate, $Al(NO_3)_3 \cdot 9H_2O$, in 150 ml of deionized distilled water; heat to effect solution. Allow to cool and make up to 200 ml.
3. Prepare dilutions of the stock vanadium solution to be used as calibration standards at the time of analysis. To each 100 ml of standard and sample alike, add 2 ml of the aluminum nitrate solution. The *calibration standards* should be prepared using the same type of acid (HCl or HNO_3) and at the same concentration as the samples for analysis.

Sample Preparation

1. The procedure for the determination of total metals as given in part 4.1.3 of the Atomic Absorption Methods section of this manual has been found to be satisfactory.

Instrumental Parameters (General)

1. Vanadium hollow cathode lamp
2. Wavelength: 318.4 nm
3. Fuel: Acetylene
4. Oxidant: Nitrous oxide
5. Type of flame: Fuel rich

Interferences

1. It has been reported that high concentrations of aluminum and titanium increase the sensitivity of vanadium. This interference can be controlled by adding excess aluminum (1000 ppm) to both samples and standards. [Talanta *15*, 871 (1968)].

Notes

1. Data to be entered into STORET must be reported as μg/l.
2. The gallic acid colorimetric method may be used (Standard Methods, 13th Edition, p 357).

Precision and Accuracy

1. In a single laboratory (MDQARL), using a mixed industrial-domestic waste effluent at concentrations of 2.0, 10 and 50 mg V/l, the standard deviations were ±0.10, ±0.1 and ±0.2, respectively. Recoveries at these levels were 100%, 95% and 97%, respectively.

ZINC

(Standard Conditions)

STORET NO. Total 01092

Optimum Concentration Range: 0.05-2 mg/l using a wavelength of 213.9 nm

Sensitivity: 0.02 mg/l

Detection Limit: 0.005 mg/l

Preparation of Standard Solution

1. Stock Solution: Carefully weigh 1.00 g of zinc metal (analytical reagent grade) and dissolve cautiously in 10 ml HNO_3. When solution is complete make up to 1 liter with deionized distilled water. 1 ml = 1 mg Zn (1000 mg/l).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The *calibration standards* should be prepared using the same type of acid (HCl or HNO_3) and at the same concentration as the samples for analysis.

Sample Preparation

1. The procedure for the determination of total metals as given in part 4.1.3 of the Atomic Absorption Methods section of this manual has been found to be satisfactory.

Instrumental Parameters

1. Zinc hollow cathode lamp
2. Wavelength: 213.9 nm
3. Fuel: Acetylene
4. Oxidant: Air
5. Type of flame: Oxidizing

Notes

1. High levels of silicon may interfere.
2. The air-acetylene flame absorbs about 25% of the energy at the 213.9 nm line.
3. The sensitivity may be increased by the use of low-temperature flames.
4. Data to be entered into STORET must be reported as μg/l.
5. The dithizone colorimetric method may be used (Standard Methods, 13th Edition, p 444).

Precision and Accuracy

1. An interlaboratory study on trace metal analyses by atomic absorption was conducted by the Quality Assurance and Laboratory Evaluation Branch of MDQARL. Six synthetic concentrates containing varying levels of aluminum,

cadmium, chromium, copper, iron, manganese, lead and zinc were added to natural water samples. The statistical results for zinc were as follows:

Number of Labs	True Values µg/liter	Mean Value µg/liter	Standard Deviation µg/liter	Accuracy as % Bias
86	281	284	97	1.2
89	310	308	114	–0.7
82	56	62	28	11.3
81	70	75	28	6.6
62	7	22	26	206
61	11	17	18	56.6

METHYLENE BLUE ACTIVE SUBSTANCES (MBAS)

(Methylene Blue Method)

STORET NO. 38260

1. Scope and Application
   1.1 This method is applicable to the measurement of methylene blue active substances (MBAS) in drinking waters, surface waters, domestic and industrial wastes. It is not applicable to measurement of surfactant-type materials in saline waters.
   1.2 It is not possible to differentiate between linear alkyl sulfonate (LAS) and alkyl benzene sulfonate (ABS) or other isomers of these types of compounds. However, LAS has essentially replaced ABS on the surfactant market so that measurable surfactant materials will probably be LAS type materials.
   1.3 The method is applicable over the range of 0.025 to 100 mg/l LAS.
2. Summary of Method
   2.1 The dye, methylene blue, in aqueous solution reacts with anionic-type surface active materials to form a blue colored salt. The salt is extractable with chloroform and the intensity of color produced is proportional to the concentration of MBAS.
3. Comments
   3.1 Materials other than man-made surface active agents which react with methylene blue are organically bound sulfates, sulfonates, carboxylates, phosphates, phenols, cyanates, thiocyanates and some inorganic ions such as nitrates and chlorides. However, the occurrence of these materials at interference levels is relatively rare and with the exception of chlorides may generally be disregarded.
   3.2 Chlorides at concentration of about 1000 mg/l show a positive interference but the degree of interference has not been quantified. For this reason the method is not applicable to brine samples.
   3.3 Naturally occurring organic materials that react with methylene blue are relatively insignificant. Except under highly unusual circumstances, measurements of MBAS in finished waters, surface waters and domestic sewages may be assumed to be accurate measurements of man-made surface active agents.
4. Precision and Accuracy
   4.1 On a sample of filtered river water, spiked with 2.94 mg LAS/liter, 110 analysts obtained a mean of 2.98 mg/liter with a standard deviation of ±0.272.

4.2 On a sample of tap water spiked with 0.48 mg LAS/liter, analysts obtained a mean of 0.49 mg/l with a standard deviation of ±0.048.

4.3 On a sample of distilled water spiked with 0.27 mg LAS/liter, 110 analysts obtained a mean of 0.24 mg/l with a standard deviation of ±0.036.

4.4 Analytical Reference Service, Water Surfactant No. 3, Study No. 32, (1968).

5. References

5.1 The procedure to be used for this determination is found in:

Standard Methods for the Examination of Water and Wastewaters, 13th Edition, p 339-342, Method No. 159A (1971).

ASTM Standards, Part 23, Water; Atmospheric Analysis, p 492, Method D2330-68 (1973).

NITROGEN, AMMONIA

(Distillation Procedure)

STORET NO. 00610

1. Scope and Application
   1.1 This distillation method covers the determination of ammonia-nitrogen exclusive of total Kjeldahl nitrogen, in drinking, surface, and saline waters, domestic and industrial wastes. It is the method of choice where economics and sample load do not warrant the use of automated equipment.
   1.2 The method covers the range from about 0.05 to 1.0 mg/l NH_3-N/l for the colorimetric procedures, from 1.0 to 25 mg/l for the titrimetric procedure, and from 0.05 to 1400 mg/l for the electrode method.
   1.3 This method is described for macro glassware; however, micro distillation equipment may also be used.
2. Summary of Method
   2.1 The sample is buffered at a pH of 9.5 with a borate buffer in order to decrease hydrolysis of cyanates and organic nitrogen compounds, and is then distilled into a solution of boric acid. The ammonia in the distillate can be determined colorimetrically by nesslerization, titrimetrically with standard sulfuric acid with the use of a mixed indicator, or potentiometrically by the ammonia electrode. The choice between the first two procedures depends on the concentration of the ammonia.
3. Sample Handling and Preservation
   3.1 Samples may be preserved with 2 ml of conc. H_2SO_4 or 40 mg $HgCl_2$ per liter and stored at 4°C.
4. Interferences
   4.1 A number of aromatic and aliphatic amines, as well as other compounds, both organic and inorganic, will cause turbidity upon the addition of Nessler reagent, so direct nesslerization (i.e., without distillation), has been discarded as an official method.
   4.2 Cyanate, which may be encountered in certain industrial effluents, will hydrolyze to some extent even at the pH of 9.5 at which distillation is carried out. Volatile alkaline compounds, such as certain ketones, aldehydes, and alcohols, may cause an off-color upon nesslerization in the distillation method. Some of these, such as formaldehyde, may be eliminated by boiling off at a low pH (approximately 2 to 3) prior to distillation and nesslerization.

4.3 Residual chlorine must also be removed by pretreatment of the sample with sodium thiosulfate before distillation.

4.4 *If the sample has been preserved with a mercury salt, the mercury ion must be complexed with sodium thiosulfate (0.2 g) prior to distillation.*

5. Apparatus

5.1 An all-glass distilling apparatus with an 800-1000 ml flask.

5.2 Spectrophotometer or filter photometer for use at 425 nm and providing a light path of 1 cm or more.

5.3 Nessler tubes: Matched Nessler tubes (APHA Standard) about 300 mm long, 17 mm inside diameter, and marked at 225 mm ±1.5 mm inside measurement from bottom.

5.4 Erlenmeyer flasks: The distillate is collected in 500 ml glass-stoppered flasks. These flasks should be marked at the 350 and the 500 ml volumes. With such marking, it is not necessary to transfer the distillate to volumetric flasks.

6. Reagents

6.1 Distilled water should be free of ammonia. Such water is best prepared by passage through an ion exchange column containing a strongly acidic cation exchange resin mixed with a strongly basic anion exchange resin. Regeneration of the column should be carried out according to the manufacturer's instructions.

NOTE 1: All solutions must be made with ammonia-free water.

6.2 Ammonium chloride, stock solution:

1.0 ml = 1.0 mg NH_3–N. Dissolve 3.819 g NH_4Cl in distilled water and bring to volume in a 1 liter volumetric flask.

6.3 Ammonium chloride, standard solution:

1.0 ml = 0.01 mg. Dilute 10.0 ml of stock solution (6.2) to 1 liter in a volumetric flask.

6.4 Boric acid solution (20 g/l): Dissolve 20 g H_3BO_3 in distilled water and dilute to 1 liter.

6.5 Mixed indicator: Mix 2 volumes of 0.2% methyl red in 95% ethyl alcohol with 1 volume of 0.2% methylene blue in 95% ethyl alcohol. This solution should be prepared fresh every 30 days.

NOTE 2: Specially denatured ethyl alcohol conforming to Formula 3A or 30 of the U.S. Bureau of Internal Revenue may be substituted for 95% ethanol.

6.6 Nessler reagent: Dissolve 100 g of mercuric iodide and 70 g of potassium iodide in a small amount of water. Add this mixture slowly, with stirring, to a cooled solution of 160 g of NaOH in 500 ml of water. Dilute the mixture to 1 liter. If this reagent is stored in a Pyrex bottle out of direct sunlight, it will remain stable for a period of up to 1 year.

NOTE 3: This reagent should give the characteristic color with ammonia within 10 minutes after addition, and should not produce a precipitate with small amounts of ammonia (0.04 mg in a 50 ml volume).

6.7 Borate buffer: Add 88 ml of 0.1 N NaOH solution to 500 ml of 0.025 M sodium tetraborate solution (5.0 g anhydrous $Na_2B_4O_7$ or 9.5 g $Na_2B_4O_7 \cdot 10H_2O$ per liter) and dilute to 1 liter.

6.8 Sulfuric acid, standard solution: (0.02 N, 1 ml = 0.28 mg NH_3–N). Prepare a stock solution of approximately 0.1 N acid by diluting 3 ml of conc. H_2SO_4 (sp. gr. 1.84) to 1 liter with CO_2-free distilled water. Dilute 200 ml of this solution to 1 liter with CO_2-free distilled water.

NOTE 4: An alternate and perhaps preferable method is to standardize the approximately 0.1 N H_2SO_4 solution against a 0.100 N Na_2CO_3 solution. By proper dilution the 0.02 N acid can then be prepared.

6.8.1 Standardize the approximately 0.02 N acid against 0.0200 N Na_2CO_3 solution. This last solution is prepared by dissolving 1.060 g anhydrous Na_2CO_3, oven-dried at 140°C, and diluting to 1000 ml with CO_2-free distilled water.

6.9 Sodium hydroxide, 1 N: Dissolve 40 g NaOH in ammonia-free water and dilute to 1 liter.

6.10 Dechlorinating reagents: A number of dechlorinating reagents may be used to remove residual chlorine prior to distillation. These include:

a. Sodium thiosulfate (1/70 N): Dissolve 3.5 g $Na_2S_2O_3 \cdot 5H_2O$) in distilled water and dilute to 1 liter. One ml of this solution will remove 1 mg/1 of residual chlorine in 500 ml of sample.

b. Sodium arsenite (1/70 N): Dissolve 1.0 g $NaAsO_2$ in distilled water and dilute to 1 liter.

7. Procedure

7.1 Preparation of equipment: Add 500 ml of distilled water to an 800 ml Kjeldahl flask. The addition of boiling chips which have been previously treated with dilute NaOH will prevent bumping. Steam out the distillation apparatus until the distillate shows no trace of ammonia with Nessler reagent.

7.2 Sample preparation: Remove the residual chlorine in the sample by adding dechlorinating agent equivalent to the chlorine residual. To 400 ml of sample add 1 N NaOH (6.9), until the pH is 9.5, checking the pH during addition with a pH meter or by use of a short range pH paper.

7.3 Distillation: Transfer the sample, the pH of which has been adjusted to 9.5, to an 800 ml Kjeldahl flask and add 25 ml of the borate buffer (6.7). Distill 300 ml at the rate of 6-10 ml/min. into 50 ml of 2% boric acid (6.4) contained in a 500 ml Erlenmeyer flask.

NOTE 5: The condenser tip or an extention of the condenser tip must extend below the level of the boric acid solution.

Dilute the distillate to 500 ml with distilled water and nesslerize an aliquot to obtain an approximate value of the ammonia-nitrogen concentration. For concentrations above 1 mg/l the ammonia should be determined titrimetrically. For concentrations below this value it is determined colorimetrically. The electrode method may also be used.

7.4 Determination of ammonia in distillate: Determine the ammonia content of the distillate titrimetrically, colorimetrically or potentiometrically as described below.

7.4.1 Titrimetric determination: Add 3 drops of the mixed indicator to the distillate and titrate the ammonia with the 0.02 N H_2SO_4, matching the end point against a blank containing the same volume of distilled water and H_3BO_3 solution.

7.4.2 Colorimetric determination: Prepare a series of Nessler tube standards as follows:

ml of Standard 1.0 ml = 0.01 mg NH_3 –N	mg NH_3 –N/50.0 ml
0.0	0.0
0.5	0.005
1.0	0.01
2.0	0.02
3.0	0.03
4.0	0.04
5.0	0.05
8.0	0.08
10.0	0.10

Dilute each tube to 50 ml with distilled water, add 1.0 ml of Nessler reagent (6.6) and mix. After 20 minutes read the optical densities at 425 nm against the blank. From the values obtained plot optical density (absorbance) vs. mg NH_3 –N for the standard curve.

7.4.3 Potentiometric determination: Consult the method entitled Nitrogen, Ammonia: Selective Ion Electrode Method in this manual.

7.4.4 It is not imperative that all standards be distilled in the same manner as the samples. It is recommended that at least two standards (a high and low) be distilled and compared to similar values on the curve to insure that the distillation technique is reliable. If distilled standards do not agree with undistilled standards the operator should find the cause of the apparent error before proceeding.

7.5 Determine the ammonia in the distillate by nesslerizing 50 ml or an aliquot diluted to 50 ml and reading the optical density at 425 nm as described above for the standards. Ammonia-nitrogen content is read from the standard curve.

8. Calculations

8.1 Titrimetric

$$\text{mg/l } NH_3-N = \frac{A \times 0.28 \times 1000}{S}$$

where:

A = ml 0.02 N H_2SO_4 used.

S = ml sample.

8.2 Spectrophotometric

$$\text{mg/l } NH_3-N = \frac{A \times 1000}{D} \times \frac{B}{C}$$

where:

A = mg NH_3-N read from standard curve.

B = ml total distillate collected, including boric acid and dilution.

C = ml distillate taken for nesslerization.

D = ml of original sample taken.

8.3 Potentiometric

$$\text{mg/l } NH_3-N = \frac{500}{D} \times A$$

where:

A = mg NH_3-N/l from electrode method standard curve.

D = ml of original sample taken.

9. Precision and Accuracy

9.1 Twenty-four analysts in sixteen laboratories analyzed natural water samples containing exact increments of an ammonium salt, with the following results:

Increment as Nitrogen, Ammonia mg N/liter	Precision as Standard Deviation mg N/liter	Accuracy as	
		Bias, %	Bias, mg N/liter
0.21	0.122	– 5.54	–0.01
0.26	0.070	–18.12	–0.05
1.71	0.244	+ 0.46	+0.01
1.92	0.279	– 2.01	–0.04

(FWPCA Method Study 2, Nutrient Analyses)

NITROGEN, AMMONIA

(Selective Ion Electrode Method)

STORET NO. 00610

1. Scope and Application
   1.1 This method is applicable to the measurement of ammonia-nitrogen in drinking, surface, and saline waters, domestic and industrial wastes.
   1.2 This method covers the range from 0.03 to 1400 mg NH_3-N/l. Color and turbidity have no effect on the measurements and distillation is not necessary.
2. Summary of Method
   2.1 The ammonia is determined potentiometrically using a selective ion ammonia electrode and a pH meter having an expanded millivolt scale or a specific ion meter.
   2.2 The ammonia electrode uses a hydrophobic gas-permeable membrane to separate the sample solution from an ammonium chloride internal solution. Ammonia in the sample diffuses through the membrane and alters the pH of the internal solution, which is sensed by a pH electrode. The constant level of chloride in the internal solution is sensed by a chloride selective ion electrode which acts as the reference electrode.
3. Sample Handling and Preservation
   3.1 Preserve by refrigeration at 4°C; analyze within 24 hours. If longer holding times are desired, preserve with 2 ml conc. H_2SO_4 per liter ($pH<2$).
4. Interferences
   4.1 Volatile amines act as a positive interference.
   4.2 Mercury interferes by forming a strong complex with ammonia. Thus the samples cannot be preserved with mercuric chloride.
5. Apparatus
   5.1 Electrometer (pH meter) with expanded mV scale or a specific ion meter.
   5.2 Ammonia selective electrode, such as Orion Model 95-10 or EIL Model 8002-2.
   5.3 Magnetic stirrer, thermally insulated, and Teflon-coated stirring bar.
6. Reagents
   6.1 Distilled water: Special precautions must be taken to insure that the distilled water is free of ammonia. This is accomplished by passing distilled water through an ion exchange column containing a strongly acidic cation exchange resin mixed with a strongly basic anion exchange resin.

6.2 Sodium hydroxide, 10N: Dissolve 400 g of sodium hydroxide in 800 ml of distilled water. Cool and dilute to 1 liter with distilled water (6.1).

6.3 Ammonium chloride, stock solution: 1.0 ml = 1.0 mg NH_3–N. Dissolve 3.819 g NH_4Cl in water and bring to volume in a 1 liter volumetric flask using distilled water (6.1).

6.4 Ammonium chloride, standard solution: 1.0 ml = 0.01 mg NH_3–N. Dilute 10.0 ml of the stock solution (6.3) to 1 liter with distilled water (6.1) in a volumetric flask.

NOTE 1: When analyzing saline waters, standards must be made up in synthetic ocean water (SOW); found in Nitrogen, Ammonia: Automated Colorimetric Phenate Method.

7. Procedure

7.1 Preparation of standards: Prepare a series of standard solutions covering the concentration range of the samples by diluting either the stock or standard solutions of ammonium chloride.

7.2 Calibration of electrometer: Place 100 ml of each standard solution in clean 150 ml beakers. Immerse electrode into standard of lowest concentration and add 1 ml of 10N sodium hydroxide solution while mixing. Keep electrode in the solution until a stable reading is obtained.

NOTE 2: The pH of the solution after the addition of NaOH *must* be above 11. *Caution*: Sodium hydroxide must not be added prior to electrode immersion, for ammonia may be lost from a basic solution.

7.3 Repeat this procedure with the remaining standards, going from lowest to highest concentration. Using semilogarithmic graph paper, plot the concentration of ammonia in mg NH_3–N/l on the log axis vs. the electrode potential developed in the standard on the linear axis, starting with the lowest concentration at the bottom of the scale.

7.4 Calibration of a specific ion meter: Follow the directions of the manufacturer for the operation of the instrument.

7.5 Sample measurement: Follow the procedure in (7.2) for 100 ml of sample in 150 ml beakers. Record the stabilized potential of each unknown sample and convert the potential reading to the ammonia concentration using the standard curve. If a specific ion meter is used, read the ammonia level directly in mg NH_3–N/l.

8. Precision and Accuracy

8.1 In a single laboratory (MDQARL), using surface water samples at concentrations of 1.00, 0.77, 0.19, and 0.13 mg NH_3–N/l, standard deviations were ±0.038, ±0.017, ±0.007, and ±0.003, respectively.

8.2 In a single laboratory (MDQARL), using surface water samples at concentrations of 0.19 and 0.13 NH_3-N/l, recoveries were 96% and 91%, respectively.

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NITROGEN, AMMONIA

(Automated Colorimetric Phenate Method)

STORET NO. 00610

1. Scope and Application

   1.1 This method covers the determination of ammonia in drinking, surface, and saline waters, domestic and industrial wastes in the range of 0.01 to 2.0 mg/l NH_3 as N. This range is for photometric measurements made at 630-660 nm in a 15 mm or 50 mm tubular flow cell. Higher concentrations can be determined by sample dilution. Approximately 20 to 60 samples per hour can be analyzed.

2. Summary of Method

   2.1 Alkaline phenol and hypochlorite react with ammonia to form indophenol blue that is proportional to the ammonia concentration. The blue color formed is intensified with sodium nitroprusside.

3. Sample Handling and Preservation

   3.1 Preservation by addition of 2 ml conc. H_2SO_4 or 40 mg $HgCl_2$ per liter and refrigeration at 4°C. Note $HgCl_2$ interference under (4.2).

4. Interferences

   4.1 In sea water, calcium and magnesium ions are present in concentrations sufficient to cause precipitation problems during the analysis. This problem is eliminated by using 5% EDTA.

   4.2 Mercury chloride, used as a preservative, gives a negative interference by complexing with the ammonia. This is overcome by adding a comparable amount of $HgCl_2$ to the ammonia standards used for the preparation of the standard curve.

   4.3 Sample turbidity and color may interfere with this method. Turbidity must be removed by filtration prior to analysis. Sample color that absorbs in the photometric range used will also interfere.

5. Apparatus

   5.1 Technicon AutoAnalyzer Unit (AAI or AAII) consisting of:

      5.1.1 Sampler.

      5.1.2 Manifold (AAI) or Analytical Cartridge (AAII).

      5.1.3 Proportioning pump.

      5.1.4 Heating bath with double delay coil (AAI).

      5.1.5 Colorimeter equipped with 15 mm tubular flow cell and 630-660 nm filters.

5.1.6 Recorder.

5.1.7 Digital printer for AAII (optional).

6. Reagents

6.1 Distilled water: Special precaution must be taken to insure that distilled water is free of ammonia. Such water is prepared by passage of distilled water through an ion exchange column comprised of a mixture of both strongly acidic cation and strongly basic anion exchange resins. The regeneration of the ion exchange column should be carried out according to the instruction of the manufacturer. NOTE 1: All solutions must be made using ammonia-free water.

6.2 Sulfuric acid 5N: Air scrubber solution. Carefully add 139 ml of conc. sulfuric acid to approximately 500 ml of ammonia-free distilled water. Cool to room temperature and dilute to 1 liter with ammonia-free distilled water.

6.3 Sodium phenolate: Using a 1 liter Erlenmeyer flask, dissolve 83 g phenol in 500 ml of distilled water. In small increments, cautiously add with agitation, 32 g of NaOH. Periodically, cool flask under water faucet. When cool, dilute to 1 liter with distilled water.

6.4 Sodium hypochlorite solution: Dilute 250 ml of a bleach solution containing 5.25% NaOCl (such as "Clorox") to 500 ml with distilled water. Available chlorine level should approximate 2 to 3%. Since "Clorox" is a proprietary product, its formulation is subject to change. The analyst must remain alert to detecting any variation in this product significant to its use in this procedure. Due to the instability of this product, storage over an extended period should be avoided.

6.5 Disodium ethylenediamine-tetraacetate (EDTA) (5%): Dissolve 50 g of EDTA (disodium salt) and approximately six pellets of NaOH in 1 liter of distilled water. NOTE 2: On salt water samples where EDTA solution does not prevent precipitation of cations, sodium potassium tartrate solution may be used to advantage. It is prepared as follows:

6.5.1 Sodium potassium tartrate solution: 10% $NaKC_4H_4O_6 \cdot 4H_2O$. To 900 ml of distilled water add 100 g sodium potassium tartrate. Add 2 pellets of NaOH and a few boiling chips, boil gently for 45 minutes. Cover, cool, and dilute to 1 liter with ammonia-free distilled water. Adjust pH to 5.2±.05 with H_2SO_4. After allowing to settle overnight in a cool place, filter to remove precipitate. Then add 1/2 ml Brij-35 (available from Technicon Corporation) solution and store in stoppered bottle.

6.6 Sodium nitroprusside (0.05%): Dissolve 0.5 g of sodium nitroprusside in 1 liter of distilled water.

6.7 Stock solution: Dissolve 3.819 g of anhydrous ammonium chloride, NH_4Cl, dried at 105°C, in distilled water, and dilute to 1000 ml. 1.0 ml = 1.0 mg NH_3-N.

6.8 Standard solution A: Dilute 10.0 ml of stock solution (6.7) to 1000 ml with distilled water. 1.0 ml = 0.01 mg NH_3-N.

6.9 Standard solution B: Dilute 10.0 ml of standard solution A (6.8) to 100.0 ml with distilled water. 1.0 ml = 0.001 mg NH_3-N.

6.10 Using standard solutions A and B, prepare the following standards in 100 ml volumetric flasks (prepare fresh daily):

NH_3-N, mg/l	ml Standard Solution/100 ml
	Solution B
0.01	1.0
0.02	2.0
0.05	5.0
0.10	10.0
	Solution A
0.20	2.0
0.50	5.0
0.80	8.0
1.00	10.0
1.50	15.0
2.00	20.0

NOTE 3: When saline water samples are analyzed, Substitute Ocean Water (SOW) should be used for preparing the above standards used for the calibration curve; otherwise, distilled water is used. If SOW is used, subtract its blank background response from the standards before preparing the standard curve.

Substitute Ocean Water (SOW)

	g/l		g/l
NaCl	24.53	$NaHCO_3$	0.20
$MgCl_2$	5.20	KBr	0.10
Na_2SO_4	4.09	H_3BO_3	0.03
$CaCl_2$	1.16	$SrCl_2$	0.03
KCl	0.70	NaF	0.003

7. Procedure

7.1 Any marked variation in acidity or alkalinity among samples should be eliminated, since the intensity of the color used to quantify the concentration is pH dependent. Likewise, the pH of the wash water and the standard ammonia solutions should approximate that of the samples. For example, if the samples have been preserved with 2 ml conc. H_2SO_4/liter, the wash water and standards should also contain 2 ml conc. H_2SO_4/liter.

7.2 For a working range of 0.01 to 2.00 mg NH_3–N/l (AAI), set up the manifold as shown in Figure 1. For a working range of .01 to 1.0 mg NH_3–N/l (AAII), set up the manifold as shown in Figure 2. Higher concentrations may be accommodated by sample dilution.

7.3 Allow both colorimeter and recorder to warm up for 30 minutes. Obtain a stable baseline with all reagents, feeding distilled water through sample line.

7.4 For the AAI system, sample at a rate of 20/hr, 1:1. For the AAII use a 60/hr 6:1 cam with a common wash.

7.5 Arrange ammonia standards in sampler in order of decreasing concentration of nitrogen. Complete loading of sampler tray with unknown samples.

7.6 Switch sample line from distilled water to sampler and begin analysis.

8. Calculations

8.1 Prepare appropriate standard curve derived from processing ammonia standards through manifold. Compute concentration of samples by comparing sample peak heights with standard curve.

9. Precision and Accuracy

9.1 In a single laboratory, (MDQARL), using surface water samples at concentrations of 1.41, 0.77, 0.59, and 0.43 mg NH_3–N/l, the standard deviation was ±0.005.

9.2 In a single laboratory (MDQARL), using surface water samples at concentrations of 0.16 and 1.44 mg NH_3–N/l, recoveries were 107% and 99%, respectively.

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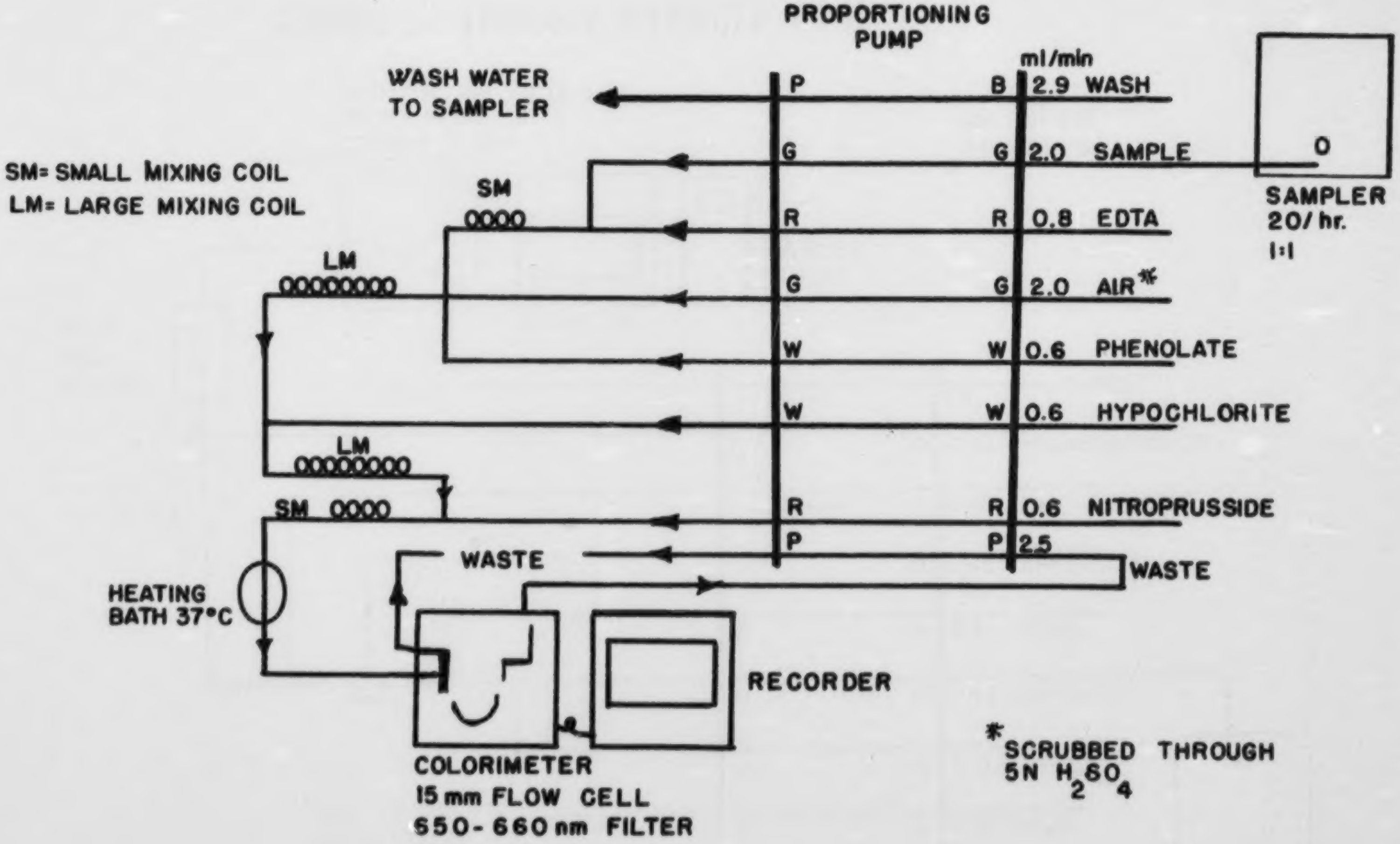
PROPORTIONING PUMP
ml/min
WASH WATER TO SAMPLER
SM= SMALL MIXING COIL
LM= LARGE MIXING COIL
SM
LM
LM
SM
P
G
R
G
W
W
R
P
B 2.9 WASH
G 2.0 SAMPLE
R 0.8 EDTA
G 2.0 AIR*
W 0.6 PHENOLATE
W 0.6 HYPOCHLORITE
R 0.6 NITROPRUSSIDE
P 2.5
WASTE
WASTE
SAMPLER 20/ hr. 1:1
HEATING BATH 37°C
RECORDER
COLORIMETER
15 mm FLOW CELL
650-660 nm FILTER
*SCRUBBED THROUGH 5N H_2SO_4

FIGURE 1 AMMONIA MANIFOLD AA I

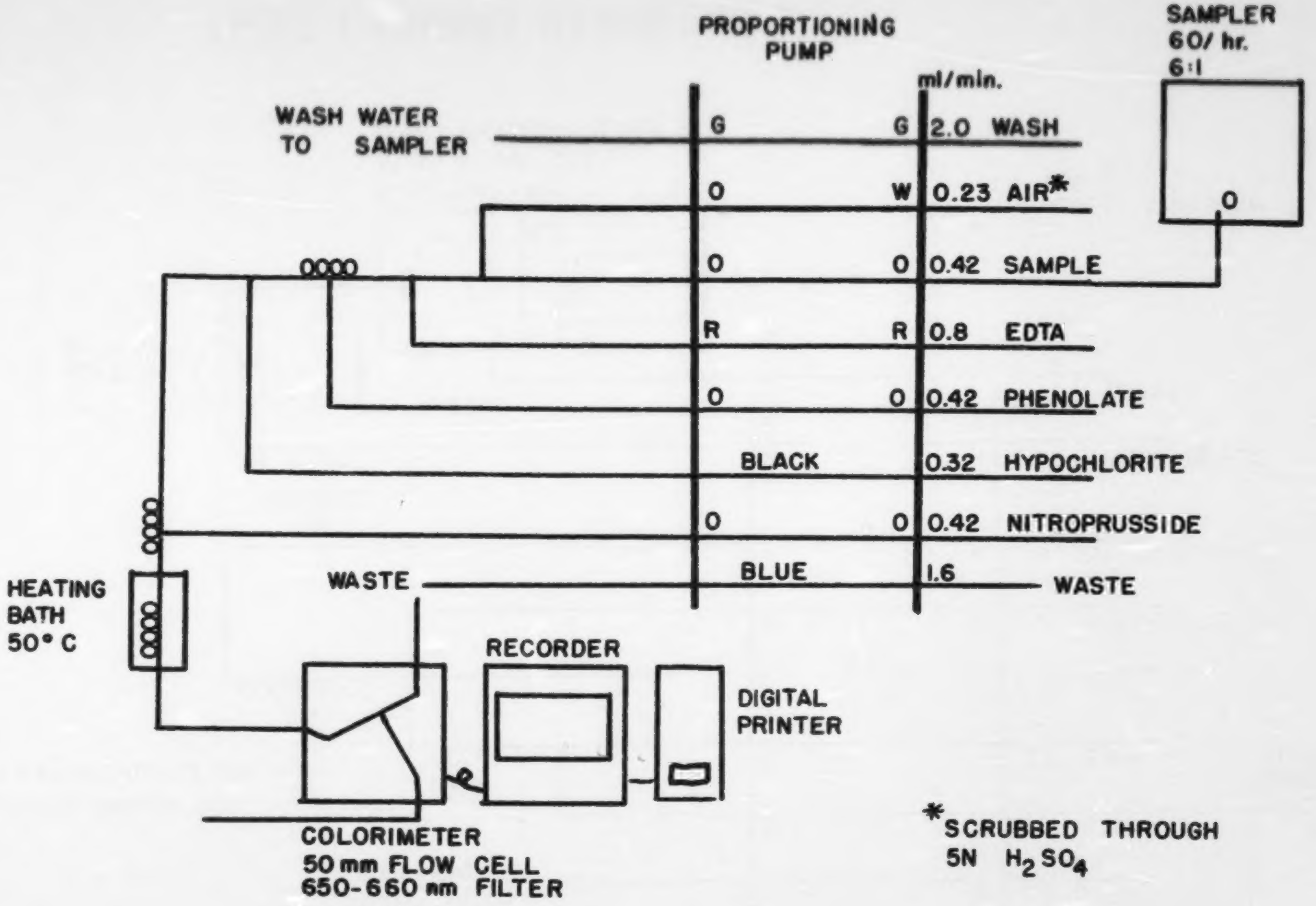
PROPORTIONING PUMP
SAMPLER
60/ hr.
6:1
ml/min.
WASH WATER TO SAMPLER
G
G 2.0 WASH
O
W 0.23 AIR*
O
O 0.42 SAMPLE
R
R 0.8 EDTA
O
O 0.42 PHENOLATE
BLACK
0.32 HYPOCHLORITE
O
O 0.42 NITROPRUSSIDE
BLUE
1.6
WASTE
WASTE
HEATING BATH 50° C
RECORDER
DIGITAL PRINTER
COLORIMETER
50 mm FLOW CELL
650-660 nm FILTER
*SCRUBBED THROUGH 5N H_2SO_4

FIGURE 2. AMMONIA MANIFOLD AA II

NITROGEN, KJELDAHL, Total

STORET NO. 00625

1. Scope and Application

1.1 This method covers the determination of total Kjeldahl nitrogen in drinking, surface, and saline waters, domestic and industrial wastes. The procedure converts nitrogen components of biological origin such as amino acids, proteins and peptides to ammonia, but may not convert the nitrogenous compounds of some industrial wastes such as amines, nitro compounds, hydrazones, oximes, semicarbazones and some refractory tertiary amines.

1.2 Three alternatives are listed for the determination of ammonia after distillation: the titrimetric method which is applicable to concentrations above 1 mg N/liter; the Nesslerization method which is applicable to concentrations below 1 mg N/liter; and the potentiometric method applicable to the range 0.05 to 1400 mg/l.

1.3 This method is described for macro and micro glassware systems.

2. Definitions

2.1 Total Kjeldahl nitrogen is defined as the sum of free-ammonia and organic nitrogen compounds which are converted to ammonium sulfate $(NH_4)_2SO_4$, under the conditions of digestion described below.

2.2 Organic Kjeldahl nitrogen is defined as the difference obtained by subtracting the free-ammonia value (cf Nitrogen, Ammonia, this manual) from the total Kjeldahl nitrogen value. This may be determined directly by removal of ammonia before digestion.

3. Summary of Method

3.1 The sample is heated in the presence of conc. sulfuric acid, K_2SO_4 and $HgSO_4$ and evaporated until SO_3 fumes are obtained and the solution becomes colorless or pale yellow. The residue is cooled, diluted, and is treated and made alkaline with a hydroxide-thiosulfate solution. The ammonia is distilled and determined after distillation by Nesslerization, titrimetry, or potentiometrically.

4. Sample Handling and Preservation

4.1 Samples may be preserved by addition of 2 ml of conc. H_2SO_4 or 40 mg $HgCl_2$ per liter and stored at 4°C. Even when preserved in this manner, conversion of organic nitrogen to ammonia may occur. Preserved samples should be analyzed as soon as possible.

5. Apparatus

5.1 Digestion apparatus: A Kjeldahl digestion apparatus with 800 or 100 ml flasks and suction takeoff to remove SO_3 fumes and water.

5.2 Distillation apparatus: The macro Kjeldahl flask is connected to a condenser and an adaptor so that the distillate can be collected. Micro Kjeldahl steam distillation apparatus is commercially available.

5.3 Spectrophotometer for use at 400 to 425 nm with a light path of 1 cm or longer.

6. Reagents

6.1 Distilled water should be free of ammonia. Such water is best prepared by the passage of distilled water through an ion exchange column containing a strongly acidic cation exchange resin mixed with a strongly basic anion exchange resin. Regeneration of the column should be carried out according to the manufacturer's instructions.

NOTE 1: All solutions must be made with ammonia-free water.

6.2 Mercuric sulfate solution: Dissolve 8 g red, mercuric oxide (HgO) in 50 ml of 1:5 sulfuric acid (10.0 ml conc. H_2SO_4: 40 ml distilled water) and dilute to 100 ml with distilled water.

6.3 Sulfuric acid-mercuric sulfate-potassium sulfate solution: Dissolve 267 g K_2SO_4 in 1300 ml distilled water and 400 ml conc. H_2SO_4. Add 50 ml mercuric sulfate solution (6.2) and dilute to 2 liters with distilled water.

6.4 Sodium hydroxide-sodium thiosulfate solution: Dissolve 500 g NaOH and 25 g $Na_2S_2O_3 \cdot 5H_2O$ in distilled water and dilute to 1 liter.

6.5 Phenolphthalein indicator solution: Dissolve 5 g phenolphthalein in 500 ml 95% ethyl alcohol or isopropanol and add 500 ml distilled water. Add 0.02 N NaOH dropwise until a faint, pink color appears.

6.6 Mixed indicator: Mix 2 volumes of 0.2% methyl red in 95% ethanol with 1 volume of 0.2% methylene blue in ethanol. Prepare fresh every 30 days.

6.7 Boric acid solution: Dissolve 20 g boric acid, H_3BO_3, in water and dilute to 1 liter with distilled water.

6.8 Sulfuric acid, standard solution: (0.02 N) 1 ml = 0.28 mg NH_3–N. Prepare a stock solution of approximately 0.1 N acid by diluting 3 ml of conc. H_2SO_4 (sp. gr. 1.84) to 1 liter with CO_2-free distilled water. Dilute 200 ml of this solution to 1 liter with CO_2-free distilled water. Standardize the approximately 0.02 N acid so prepared against 0.0200 N Na_2CO_3 solution. This last solution is prepared by dissolving 1.060 g anhydrous Na_2CO_3, oven-dried at 140°C, and diluting to 1 liter with CO_2-free distilled water.

NOTE 2: An alternate and perhaps preferable method is to standardize the approximately 0.1 N H_2SO_4 solution against a 0.100 N $NaCO_3$ solution. By proper dilution the .02 N acid can then be prepared.

6.9 Ammonium chloride, stock solution: 1.0 ml = 1.0 mg NH_3–N. Dissolve 3.819 g NH_4Cl in water and make up to 1 liter in a volumetric flask with distilled water.

6.10 Ammonium chloride, standard solution: 1.0 ml = 0.01 mg NH_3–N. Dilute 10.0 ml of the stock solution (6.9) with distilled water to 1 liter in a volumetric flask.

6.11 Nessler reagent: Dissolve 100 g of mercuric iodide and 70 g potassium iodide in a small volume of distilled water. Add this mixture slowly, with stirring, to a cooled solution of 160 g of NaOH in 500 ml of distilled water. Dilute the mixture to 1 liter. The solution is stable for at least one year if stored in a pyrex bottle out of direct sunlight.

NOTE 3: Reagents 6.8, 6.9, 6.10, and 6.11 are identical to reagents 6.8, 6.2, 6.3, and 6.6 described under Nitrogen, Ammonia (Distillation Procedure).

7. Procedure

7.1 The distillation apparatus should be pre-steamed before use by distilling a 1:1 mixture of distilled water and sodium hydroxide-sodium thiosulfate solution (6.4) until the distillate is ammonia-free. This operation should be repeated each time the apparatus is out of service long enough to accumulate ammonia (usually 4 hours or more).

7.2 Macro Kjeldahl system

7.2.1 Place a measured sample or the residue from the distillation in the ammonia determination (for Organic Kjeldahl only) into an 800 ml Kjeldahl flask. The sample size can be determined from the following table:

Kjeldahl Nitrogen in Sample, mg/l	Sample Size ml
0 – 5	500
5 – 10	250
10 – 20	100
20 – 50	50.0
50 – 500	25.0

Dilute the sample, if required, to 500 ml with distilled water, and add 100 ml sulfuric acid-mercuric sulfate-potassium sulfate solution (6.3)

(Note 4), and evaporate the mixture in the Kjeldahl apparatus until SO_3 fumes are given off and the solution turns colorless or *pale yellow*. Continue heating for 30 additional minutes. Cool the residue and add 300 ml distilled water.

NOTE 4: Digesting the sample with 1 Kel-Pac (Olin-Matheson) and 20 ml conc. H_2SO_4 is acceptable. Cut the end from the package and empty the contents into the digestion flask; discard the container.

7.2.2 Make the digestate alkaline by careful addition of 100 ml of sodium hydroxide-thiosulfate solution (6.4) without mixing.

NOTE 5: Slow addition of the heavy caustic solution down the tilted neck of the digestion flask will cause heavier solution to underlay the aqueous sulfuric acid solution without loss of free-ammonia. Do not mix until the digestion flask has been connected to the distillation apparatus.

7.2.3 Connect the Kjeldahl flask to the condenser with the tip of condenser (or an extension of the condenser tip) below the level of the boric acid solution (6.7) in the receiving flask.

7.2.4 Distill 300 ml at the rate of 6-10 ml/min., into 50 ml of 2% boric acid (6.7) contained in a 500 ml Erlenmeyer flask.

7.2.5 Dilute the distillate to 500 ml in the flask. These flasks should be marked at the 350 and the 500 ml volumes. With such marking, it is not necessary to transfer the distillate to volumetric flasks. For concentrations above 1 mg/l, the ammonia can be determined titrimetrically. For concentrations below this value, it is determined colorimetrically. The potentiometric method is applicable to the range 0.05 to 1400 mg/l.

7.3 Micro Kjeldahl system

7.3.1 Place 50.0 ml of sample or an aliquot diluted to 50 ml in a 100 ml Kjeldahl flask and add 10 ml sulfuric acid-mercuric sulfate-potassium sulfate solution (6.3). Evaporate the mixture in the Kjeldahl apparatus until SO_3 fumes are given off and the solution turns colorless or pale yellow. Then digest for an additional 30 minutes. Cool the residue and add 30 ml distilled water.

7.3.2 Make the digestate alkaline by careful addition of 10 ml of sodium hydroxide-thiosulfate solution (6.4) without mixing. Do not mix until the digestion flask has been connected to the distillation apparatus.

7.3.3 Connect the Kjeldahl flask to the condenser with the tip of condenser or an extension of the condenser tip below the level of the boric acid solution (6.7) in the receiving flask or 50 ml short-form Nessler tube.

7.3.4 Steam distill 30 ml at the rate of 6-10 ml/min., into 5 ml of 2% boric acid (6.7).

7.3.5 Dilute the distillate to 50 ml. For concentrations above 1 mg/l the ammonia can be determined titrimetrically. For concentrations below this value, it is determined colorimetrically. The potentiometric method is applicable to the range 0.05 to 1400 mg/l.

7.4 Determination of ammonia in distillate: Determine the ammonia content of the distillate titrimetrically, colorimetrically, or potentiometrically, as described below.

7.4.1 Titrimetric determination: Add 3 drops of the mixed indicator (6.6) to the distillate and titrate the ammonia with the 0.02 N H_2SO_4, (6.8), matching the endpoint against a blank containing the same volume of distilled water and H_3BO_3 (6.7) solution.

7.4.2 Colorimetric determination: Prepare a series of Nessler tube standards as follows:

ml of Standard 1.0 ml = 0.01 mg NH_3–N	mg NH_3–N/50.0 ml
0.0	0.0
0.5	0.005
1.0	0.010
2.0	0.020
4.0	0.040
5.0	0.050
8.0	0.080
10.0	0.10

Dilute each tube to 50 ml with ammonia free water, add 1 ml of Nessler Reagent (6.11) and mix. After 20 minutes read the optical densities at 425 nm against the blank. From the values obtained for the standards plot optical density (absorbance) vs. mg NH_3-N for the standard curve. Develop color in the 50 ml diluted distillate in exactly the same manner and read mg NH_3-N from the standard curve.

7.4.3 Potentiometric determination: Consult the method entitled Nitrogen, Ammonia: Selective Ion Electrode Method, in this manual.

7.4.4 It is not imperative that all standards be treated in the same manner as the samples. It is recommended that at least 2 standards (a high and low) be digested, distilled, and compared to similar values on the curve to insure that the digestion-distillation technique is reliable. If treated standards do not agree with untreated standards the operator should find the cause of the apparent error before proceeding.

8. Calculation

8.1 If the titrimetric procedure is used calculate Total Kjeldahl Nitrogen, in mg/l, in the original sample as follows:

$$\text{Total Kjeldahl nitrogen, mg/l} = \frac{(A-B)N \times F \times 1000}{S}$$

where:

A = milliliters of standard 0.020 N H_2SO_4 solution used in titrating sample.
B = milliliters of standard 0.020 N H_2SO_4 solution used in titrating blank.
N = normality of sulfuric acid solution.
F = milliequivalent weight of nitrogen (14 mg).
S = milliliters of sample digested.

If the sulfuric acid is exactly 0.02 N the formula is shortened to:

$$\text{TKN, mg/l} = \frac{(A-B) \times 280}{S}$$

8.2 If the Nessler procedure is used, calculate the Total Kjeldahl Nitrogen, in mg/l, in the original sample as follows:

$$\text{TKN, mg/l} = \frac{A \times 1000}{D} \times \frac{B}{C}$$

where:

A = mg NH_3-N read from curve.
B = ml total distillate collected including the H_3BO_3.
C = ml distillate taken for Nesslerization.
D = ml of original sample taken.

8.3 Calculate Organic Kjeldahl Nitrogen in mg/l, as follows:

Organic Kjeldahl Nitrogen = TKN $-(NH_3-N.)$

8.4 Potentiometric determination: For a distillate volume of 500 ml, calculate Total Kjeldahl Nitrogen, in mg/1, in the original sample as follows:

$$\text{TKN, mg/l} = \frac{500}{D} \times A$$

where:

A = mg NH_3–N/l from electrode method standard curve.

D = ml of original sample taken.

9. Precision

9.1 Thirty-one analysts in twenty laboratories analyzed natural water samples containing exact increments of organic nitrogen, with the following results:

Increment as Nitrogen, Kjeldahl mg N/liter	Precision as Standard Deviation mg N/liter	Accuracy as Bias, %	Bias, mg N/liter
0.20	0.197	+15.54	+0.03
0.31	0.247	+ 5.45	+0.02
4.10	1.056	+ 1.03	+0.04
4.61	1.191	– 1.67	–0.08

(FWPCA Method Study 2, Nutrient Analyses)

NITROGEN, KJELDAHL, TOTAL

(Automated Phenate Method)

STORET NO. 00625

1. Scope and Application
   1.1 This automated method may be used to determine Kjeldahl nitrogen in surface and saline waters. The applicable range is 0.05 to 2.0 mg N/l. Approximately 20 samples per hour can be analyzed.
2. Summary of Method
   2.1 The sample is automatically digested with a sulfuric acid solution containing potassium sulfate and mercuric sulfate as a catalyst to convert organic nitrogen to ammonium sulfate. The solution is then automatically neutralized with sodium hydroxide solution and treated with alkaline phenol reagent and sodium hypochlorite reagent. This treatment forms a blue color designated as indophenol. Sodium nitroprusside, which increases the intensity of the color, is added to obtain necessary sensitivity for measurement of low level nitrogen.
3. Definitions
   3.1 Total Kjeldahl nitrogen is defined as the sum of free-ammonia and of organic nitrogen compounds which are converted to $(NH_4)_2SO_4$ under the conditions of digestion which are specified below.
   3.2 Organic Kjeldahl nitrogen is defined as the difference obtained by subtracting the free-ammonia value from the total Kjeldahl nitrogen value. Also, organic Kjeldahl nitrogen may be determined directly by removal of ammonia before digestion.
4. Sample Handling and Preservation
   4.1 Samples may be preserved by addition of 2 ml of conc. H_2SO_4 or 40 mg $HgCl_2$ per liter and refrigeration at 4°C.
5. Interferences
   5.1 Iron and chromium ions tend to catalyze while copper ions tend to inhibit the indophenol color reaction.
6. Apparatus
   6.1 Technicon AutoAnalyzer consisting of:
      6.1.1 Sampler II, equipped with continuous mixer.
      6.1.2 Two proportioning pumps.

6.1.3 Manifold I.

6.1.4 Manifold II.

6.1.5 Continuous digester.

6.1.6 Planetary pump.

6.1.7 Five-gallon Carboy fume-trap.

6.1.8 80°C Heating bath.

6.1.9 Colorimeter equipped with 50 mm tubular flow cell and 630 nm filters.

6.1.10 Recorder equipped with range expander.

6.1.11 Vacuum pump.

7. Reagents

7.1 Distilled water: Special precaution must be taken to insure that distilled water is free of ammonia. Such water is prepared by passage of distilled water through an ion exchange column comprised of a mixture of both strongly acidic cation and strongly basic anion exchange resins. Furthermore, since organic contamination may interfere with this analysis, use of the resin Dowex XE-75 or equivalent which also tends to remove organic impurities is advised. The regeneration of the ion exchange column should be carried out according to the instruction of the manufacturer.

NOTE 1: All solutions must be made using ammonia-free water.

7.2 Sulfuric acid: As it readily absorbs ammonia, special precaution must also be taken with respect to its use. Do not store bottles reserved for this determination in areas of potential ammonia contamination.

7.3 EDTA (2% solution): Dissolve 20 g disodium ethylenediamine tetraacetate in 1 liter of distilled water. Adjust pH to 10.5-11 with NaOH (7.4).

7.4 Sodium hydroxide (30% solution): Dissolve 300 g NaOH in 1 liter of distilled water.

NOTE 2: The 30% sodium hydroxide should be sufficient to neutralize the digestate. In rare cases it may be necessary to increase the concentration of sodium hydroxide in this solution to insure neutralization of the digested sample in the manifold at the water jacketed mixing coil.

7.5 Sodium nitroprusside, (0.05% solution): Dissolve 0.5 g $Na_2Fe(CN)_5NO \cdot 2H_2O$ in 1 liter distilled water.

7.6 Alkaline phenol reagent: Pour 550 ml liquid phenol (88-90%) slowly with mixing into 1 liter of 40% (400 g per liter) NaOH. Cool and dilute to 2 liters with distilled water.

7.7 Sodium hypochlorite (1% solution): Dilute commercial "Clorox"–200 ml to 1 liter with distilled water. Available chlorine level should be approximately 1%. Due to the instability of this product, storage over an extended period should be avoided.

7.8 Digestant mixture: Place 2 g red HgO in a 2 liter container. Slowly add, with stirring, 300 ml of acid water (100 ml H_2SO_4 + 200 ml H_2O) and stir until cool. Add 100 ml 10% (10 g per 100 ml) K_2SO_4. Dilute to 2 liters with conc. sulfuric acid (approximately 500 ml at a time, allowing time for cooling). Allow 4 hours for the precipitate to settle or filter through glass fiber filter.

7.9 Stock solutions: Dissolve 4.7619 g of pre-dried (1 hour at 105°C) ammonium sulfate in distilled water and dilute to 1.0 liter in a volumetric flask. 1.0 ml = 1.0 mg N.

7.10 Standard solution: Dilute 10.0 ml of stock solution (7.9) to 1000 ml. 1.0 ml = 0.01 mg N.

7.11 Using the standard solution (7 .10), prepare the following standards in 100 ml volumetric flasks:

Conc., mg N/l	ml Standard Solution/100 ml
0.00	0.0
0.05	0.5
0.10	1.0
0.20	2.0
0.40	4.0
0.60	6.0
0.80	8.0
1.00	10.0
1.50	15.0
2.00	20.0

8. Procedure

8.1 Set up manifolds as shown in Figures 1, 2, and 3.

8.1.1 In the operation of manifold No. 1, the control of four key factors is required to enable manifold No. 2 to receive the mandatory representative feed. First, the digestant flowing into the pulse chamber (PC-1) must be bubble free; otherwise, air will accumulate in A-7, thus altering the ratio of sample to digestant in digestor. Second, in maintaining even flow from the digestor helix, the peristaltic pump must be adjusted to cope with differences in density of the digestate and the wash water. Third, the sample pick-up rate from the helix must be precisely adjusted to insure that the entire sample is aspirated into the mixing chamber. And finally, the contents of the "Mixing Chamber" must be kept homogeneous by the proper adjustment of the air bubbling rate.

8.1.2 In the operation of manifold No. 2, it is important in the neutralization of the digested sample to adjust the concentration of the NaOH so that the waste from the C-3 debubbler is slightly acid to Hydrion B paper.

8.1.3 The digestor temperature is 390°C for the first stage and 360°C for the second and third stages.

8.2 Allow both colorimeter and recorder to warm up for 30 minutes. Run a baseline with all reagents, feeding distilled water through the sample line. Adjust dark current and operative opening on colorimeter to obtain stable baseline.

8.3 Set sampling rate of Sampler II at 20 samples per hour, using a sample to wash ratio of 1 to 2 (1 minute sample, 2 minute wash).

8.4 Arrange various standards in sampler cups in order of increasing concentration. Complete loading of sampler tray with unknown samples.

8.5 Switch sample line from distilled water to sampler and begin analysis.

9. Calculation

9.1 Prepare standard curve by plotting peak heights of processed standards against concentration values. Compute concentration of samples by comparing sample peak heights with standard curve.

9.2 Any sample that has a computed concentration that is less than 10% of the sample run immediately prior to it must be rerun.

10. Precision and Accuracy

10.1 Six laboratories analyzed four natural water samples containing exact increments of organic nitrogen compounds, with the following results:

Increment as Kjeldahl-Nitrogen mg N/liter	Precision as Standard Deviation Kjeldahl–N mg N/liter	Accuracy as	
		Bias, %	Bias, mg N/liter
1.89	0.54	–24.6	–0.46
2.18	0.61	–28.3	–0.62
5.09	1.25	–23.8	–1.21
5.81	1.85	–21.9	–1.27

(FWQA Method Study 4, Automated Methods – In preparation).

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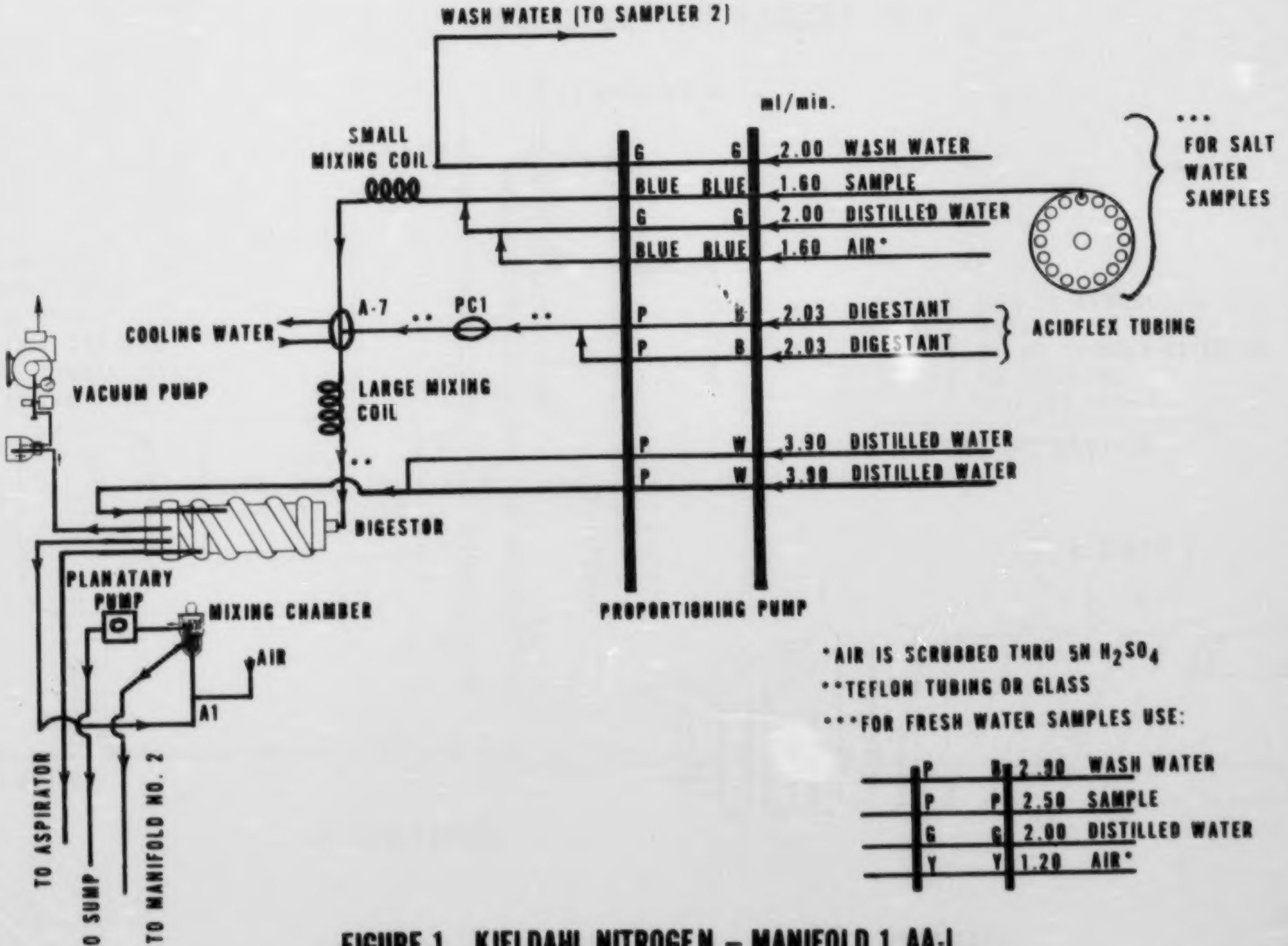
3. B. O'Connor, Dobbs, Villiers, and Dean, "Laboratory Distillation of Municipal Waste Effluents". JWPCF *39*, R 25, 1967.


WASH WATER (TO SAMPLER 2)
ml/min.
SMALL MIXING COIL
G
G
2.00
WASH WATER
BLUE
BLUE
1.60
SAMPLE
G
G
2.00
DISTILLED WATER
BLUE
BLUE
1.60
AIR*
FOR SALT WATER SAMPLES
***
A-7
PC1
COOLING WATER
P
B
2.03
DIGESTANT
P
B
2.03
DIGESTANT
ACIDFLEX TUBING
VACUUM PUMP
LARGE MIXING COIL
P
W
3.90
DISTILLED WATER
P
W
3.90
DISTILLED WATER
DIGESTOR
PLANATARY PUMP
MIXING CHAMBER
AIR
A1
PROPORTIONING PUMP
TO ASPIRATOR
TO SUMP
TO MANIFOLD NO. 2
P
B
2.90
WASH WATER
P
P
2.50
SAMPLE
G
G
2.00
DISTILLED WATER
Y
Y
1.20
AIR*

*AIR IS SCRUBBED THRU 5N H_2SO_4

**TEFLON TUBING OR GLASS

***FOR FRESH WATER SAMPLES USE:

FIGURE 1. KJELDAHL NITROGEN – MANIFOLD 1 AA-I

CONTINUOUS DIGESTER & MIXING CHAMBER ASSEMBLY

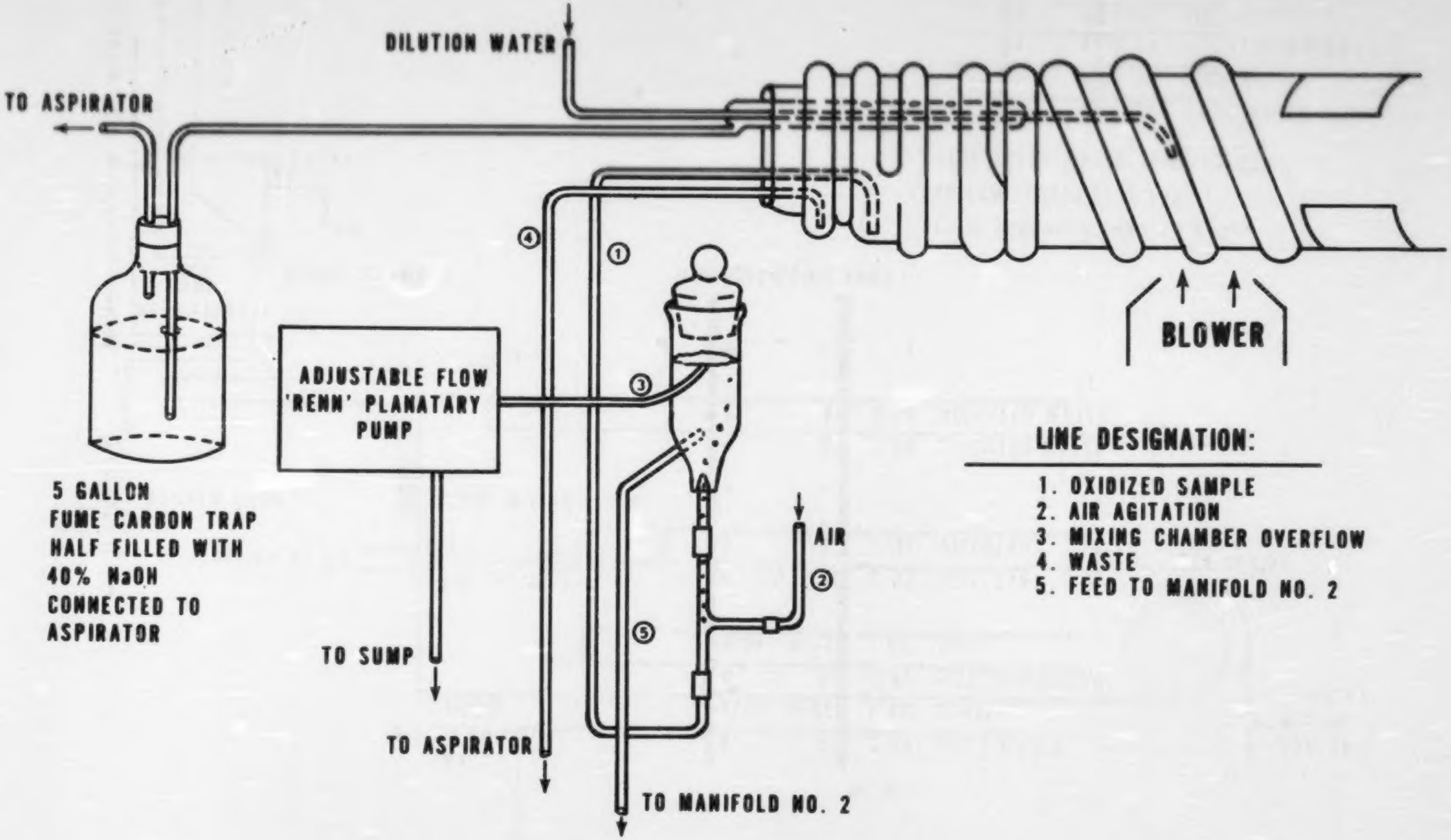

DILUTION WATER
TO ASPIRATOR
BLOWER
ADJUSTABLE FLOW
'RENN' PLANATARY
PUMP
5 GALLON
FUME CARBON TRAP
HALF FILLED WITH
40% NaOH
CONNECTED TO
ASPIRATOR
TO SUMP
TO ASPIRATOR
AIR
TO MANIFOLD NO. 2
①
②
③
④
⑤
LINE DESIGNATION:
1. OXIDIZED SAMPLE
2. AIR AGITATION
3. MIXING CHAMBER OVERFLOW
4. WASTE
5. FEED TO MANIFOLD NO. 2

FIGURE 2. KJELDAHL NITROGEN AA-I

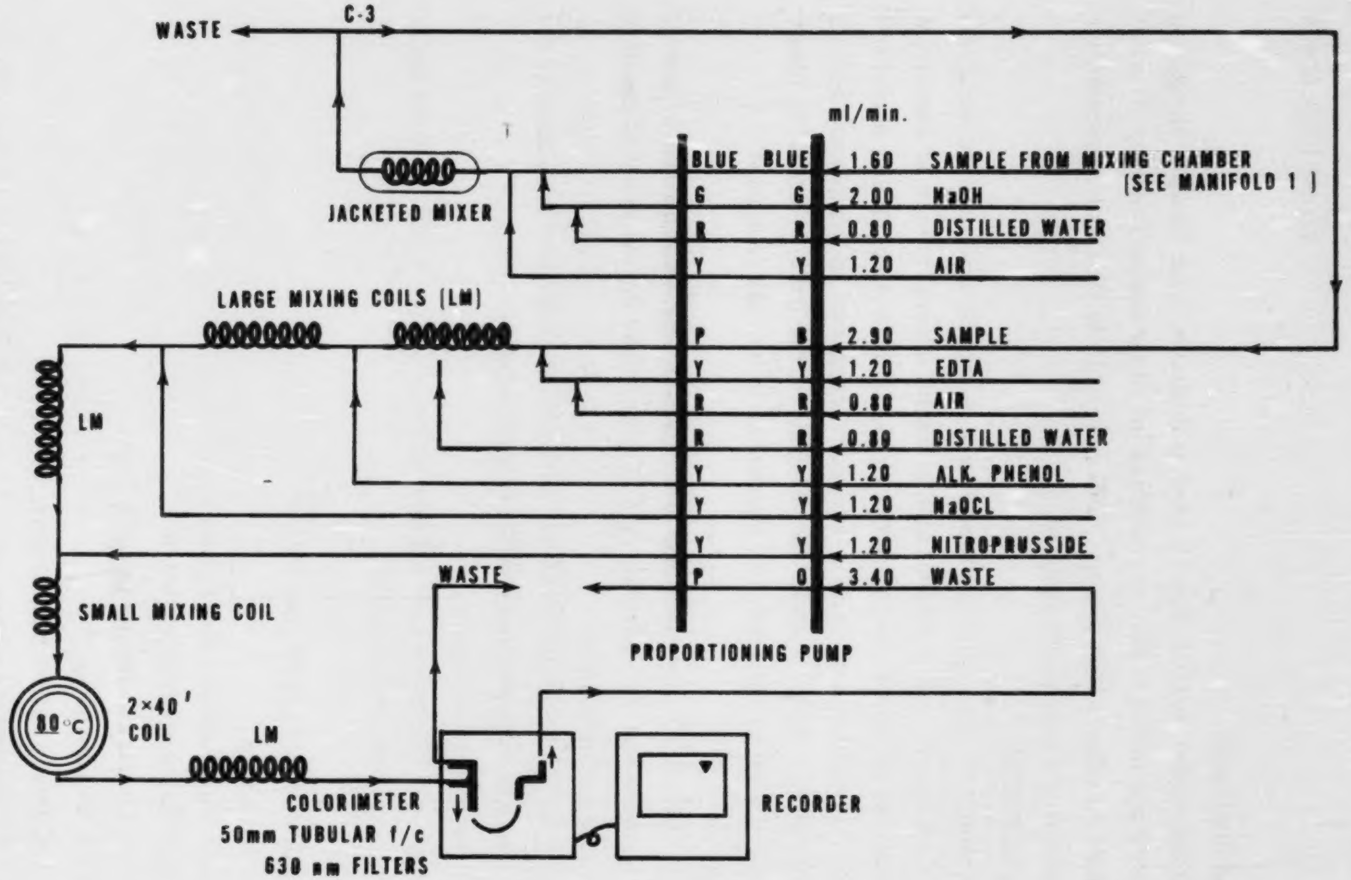

WASTE
C-3
ml/min.
JACKETED MIXER
BLUE BLUE 1.60 SAMPLE FROM MIXING CHAMBER (SEE MANIFOLD 1)
G G 2.00 NaOH
R R 0.80 DISTILLED WATER
Y Y 1.20 AIR
LARGE MIXING COILS (LM)
P B 2.90 SAMPLE
Y Y 1.20 EDTA
R R 0.80 AIR
R R 0.80 DISTILLED WATER
Y Y 1.20 ALK. PHENOL
Y Y 1.20 NaOCL
Y Y 1.20 NITROPRUSSIDE
P O 3.40 WASTE
LM
WASTE
SMALL MIXING COIL
PROPORTIONING PUMP
80°C
2×40′ COIL
LM
COLORIMETER
50mm TUBULAR f/c
630 nm FILTERS
RECORDER

FIGURE 3. KJELDAHL NITROGEN MANIFOLD 2. AA-I

NITROGEN, KJELDAHL, TOTAL
(Automated Selenium Method)

STORET NO. 00625

1. Scope and Application

   1.1 This automated method may be used to determine total Kjeldahl nitrogen in drinking and surface waters, domestic and industrial wastes. This method cannot be used on saline waters. The applicable range is 0.1 to 10.0 mg/l. Approximately 15 samples per hour can be analyzed.

2. Summary of Method

   2.1 The sample is automatically digested with a sulfuric acid solution containing selenium dioxide and perchloric acid to convert organic nitrogen to ammonium sulfate. The solution is then treated with sodium hydroxide, alkaline phenol and sodium hypochlorite to form a blue color designated as indophenol. Sodium nitroprusside, which increases the intensity of the color, is added to obtain necessary sensitivity and eliminate interference of iron and manganese.

3. Definitions

   3.1 Total Kjeldahl nitrogen is defined as the sum of free ammonia and of organic compounds which are converted to $(NH_4)_2SO_4$ under the conditions of digestion which are specified below.

   3.2 Organic Kjeldahl nitrogen is defined as the difference obtained by subtracting the free ammonia from the total Kjeldahl nitrogen value.

4. Sample Handling and Preservation

   4.1 Samples may be preserved by addition of 2 ml of conc. H_2SO_4 or 40 mg $HgCl_2$ per liter and refrigeration at 4°C.

5. Apparatus

   5.1 Technicon AutoAnalyzer consisting of:

      5.1.1 Sampler.

      5.1.2 Two manifolds (See Figures 1 and 2 or 3).

      5.1.3 Two proportioning pumps.

      5.1.4 Continuous digestor (speed 6.7 rpm).

      5.1.5 Vacuum pump.

      5.1.6 Two five gallon glass carboys.

      5.1.7 Colorimeter equipped with a 15 or 50 mm flow cell and a 630 or 650 nm filter.

      5.1.8 Recorder.

6. Reagents for AAI

6.1 Ammonia-free water: Ammonia-free water is prepared by passage of distilled water through an ion exchange column comprised of a mixture of both strongly acidic cation and strongly basic anion exchange resins. Dowex XE-75 or equivalent is advised.

NOTE 1: All solutions must be made using ammonia-free water.

6.2 Sulfuric acid: As it readily absorbs ammonia, special precaution must also be taken with respect to its use. Do not store bottles reserved for this determination in areas of potential ammonia contamination.

6.3 Digestion mixture: Dissolve 3 g selenium dioxide in 50 ml of distilled water. Add 20 ml of perchloric acid (67-70%). Dilute slowly to 1 liter with conc. sulfuric acid (6.2).

6.4 Sodium hydroxide-tartrate: Dissolve 350 g NaOH and 50 g of $KNaC_4H_4O_6 \cdot 4H_2O$ in 700 ml of distilled water. Allow to cool and dilute to 1 liter.

6.5 Alkaline phenol: Dissolve 120 g of phenol in 500 ml of distilled water. Add 31 g NaOH. Dilute to 1 liter with distilled water.

6.6 Sodium hypochlorite: Dilute 200 ml of fresh "Clorox" to 1 liter with distilled water. *Caution:* Do not store "Clorox" for extended periods; it is not stable.

6.7 Sodium nitroprusside: Dissolve 0.5 g of sodium nitroprusside in 1 liter of distilled water.

6.8 Stock solution: Dissolve 3.819 g of predried (1 hour at 105°C) ammonium chloride in distilled water and dilute to 1 liter in a volumetric flask. 1.0 ml = 1.0 mg N.

6.9 Standard solution A: Dilute 100.0 ml of stock solution (6.8) to 1 liter in a volumetric flask. 1.0 ml = 0.10 mg N.

6.10 Standard solution B: Dilute 10.0 ml of standard solution A (6.9) to 100.0 ml. 1.0 ml = 0.01 mg N. (See dilution table on p. 192.)

7. Reagents for AAII

All reagents listed for AAI, Section 6, except the digestion mixture and the sodium hydroxide-tartrate solution.

7.1 Digestion mixture: Dissolve 3 g selenium dioxide in 100 ml of distilled water. Add 3 ml of perchloric acid (67-70%). Dilute slowly to 1 liter with conc. sulfuric acid (6.2).

7.2 Sodium hydroxide-tartrate: Dissolve 270 g NaOH and 50 g $KNaC_4H_4O_6 \cdot 4H_2O$ in 700 ml of distilled water. Allow to cool and dilute to 1 liter.

ml of Standard Solution/100 ml	Conc. mg N/l
Solution B	
1.0	0.1
2.0	0.2
5.0	0.5
10.0	1.0
Solution A	
2.0	2.0
5.0	5.0
8.0	8.0
10.0	10.0

8. Procedure

8.1 Set up manifolds as shown in Figures 1 and 2 or 3.

8.1.1 In the operation of manifold No. 1, the acidflex tubing should be in good condition at all times. The life of the tubing can be extended by air drying after each run.

8.1.2 The digestor temperature is 390-400°C (4.2 ampere) for the first stage and 370-380°C (7.0 ampere) for the second and third stages.

8.2 Allow digestor, colorimeter and recorder to warm up for 30 minutes. Run a baseline with all reagents, feeding distilled water through the sample line.

8.3 Sampling rate:

8.3.1 Large sampler – use 1 minute, 15 second sample and 2 minute, 30 second wash.

8.3.2 Sampler II or IV – set sampling rate at 20 samples per hour using a sample to wash ratio of 1:2 (1 minute sample, 2 minute wash).

8.4 Arrange series of standards in sampler cups or test tubes in order of decreasing concentration.

8.5 Switch sample line from distilled water sample and begin analysis.

NOTE 2: During sampling, sample must be agitated.

9. Calculations

9.1 Prepare standard curve by plotting peak heights of processed standard against concentration values. Compute concentration of samples by comparing sample peak heights with standard curve.

10. Precision and Accuracy

10.1 In a single laboratory (MDQARL), using surface water samples of concentrations of 0.32, 1.05, 1.26, and 4.30 mg N/l, the precision was ±0.09, ±0.05, ±0.09, and ±0.14 mg N/l, respectively.

10.2 In a single laboratory (MDQARL), using a variety of domestic and industrial wastes ranging from 23 to 68 mg N/l, recoveries were 91 to 102%.

Bibliography

1. Technicon AutoAnalyzer Methodology Industrial Method, 30-69A, (1969).

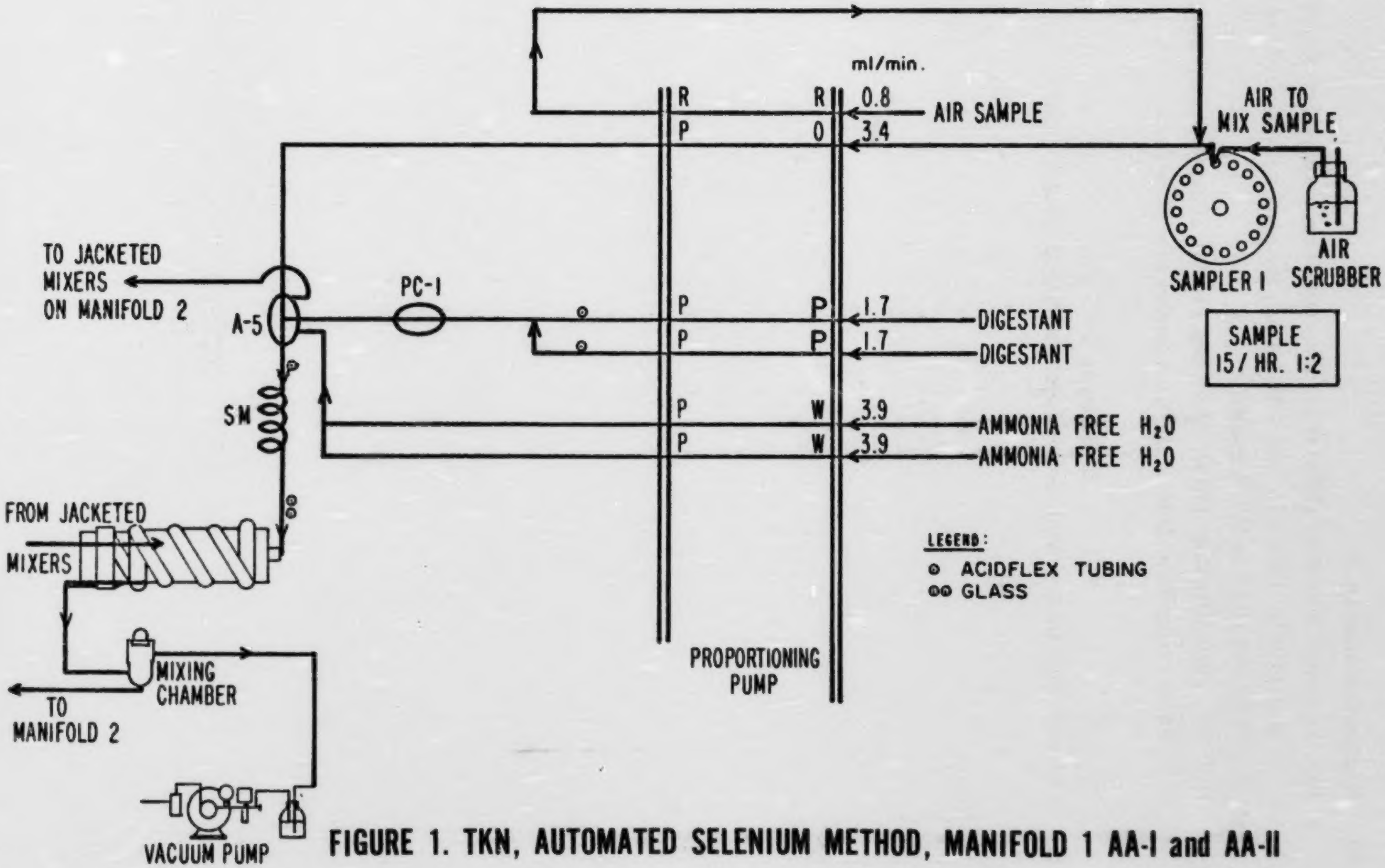

ml/min.
R
R
0.8
AIR SAMPLE
P
0
3.4
AIR TO
MIX SAMPLE
SAMPLER I
AIR
SCRUBBER
SAMPLE
15/ HR. 1:2
TO JACKETED
MIXERS
ON MANIFOLD 2
A-5
PC-1
P
P
1.7
DIGESTANT
P
P
1.7
DIGESTANT
SM
P
W
3.9
AMMONIA FREE H_2O
P
W
3.9
AMMONIA FREE H_2O
FROM JACKETED
MIXERS
MIXING
CHAMBER
TO
MANIFOLD 2
LEGEND:
⊙ ACIDFLEX TUBING
⊙⊙ GLASS
PROPORTIONING
PUMP
VACUUM PUMP

FIGURE 1. TKN, AUTOMATED SELENIUM METHOD, MANIFOLD 1 AA-I and AA-II

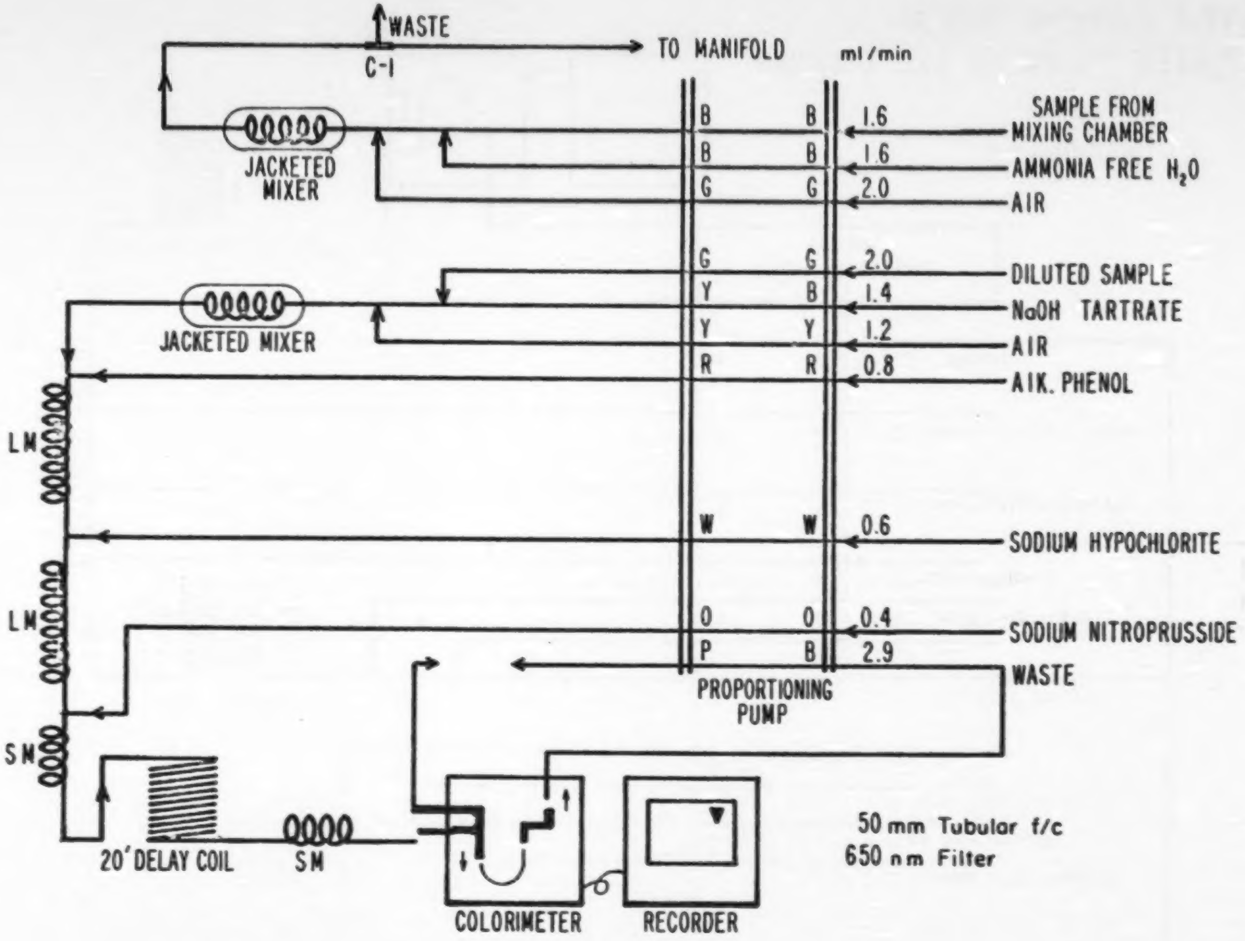

WASTE
C-I
TO MANIFOLD
ml/min
JACKETED MIXER
JACKETED MIXER
B B 1.6 SAMPLE FROM MIXING CHAMBER
B B 1.6 AMMONIA FREE H_2O
G G 2.0 AIR
G G 2.0 DILUTED SAMPLE
Y B 1.4 NaOH TARTRATE
Y Y 1.2 AIR
R R 0.8 AIK. PHENOL
W W 0.6 SODIUM HYPOCHLORITE
O O 0.4 SODIUM NITROPRUSSIDE
P B 2.9 WASTE
PROPORTIONING PUMP
LM
LM
SM
20' DELAY COIL
SM
COLORIMETER
RECORDER
50 mm Tubular f/c
650 nm Filter

FIGURE 2. TKN, AUTOMATED SELENIUM METHOD, MANIFOLD 2 AA-I

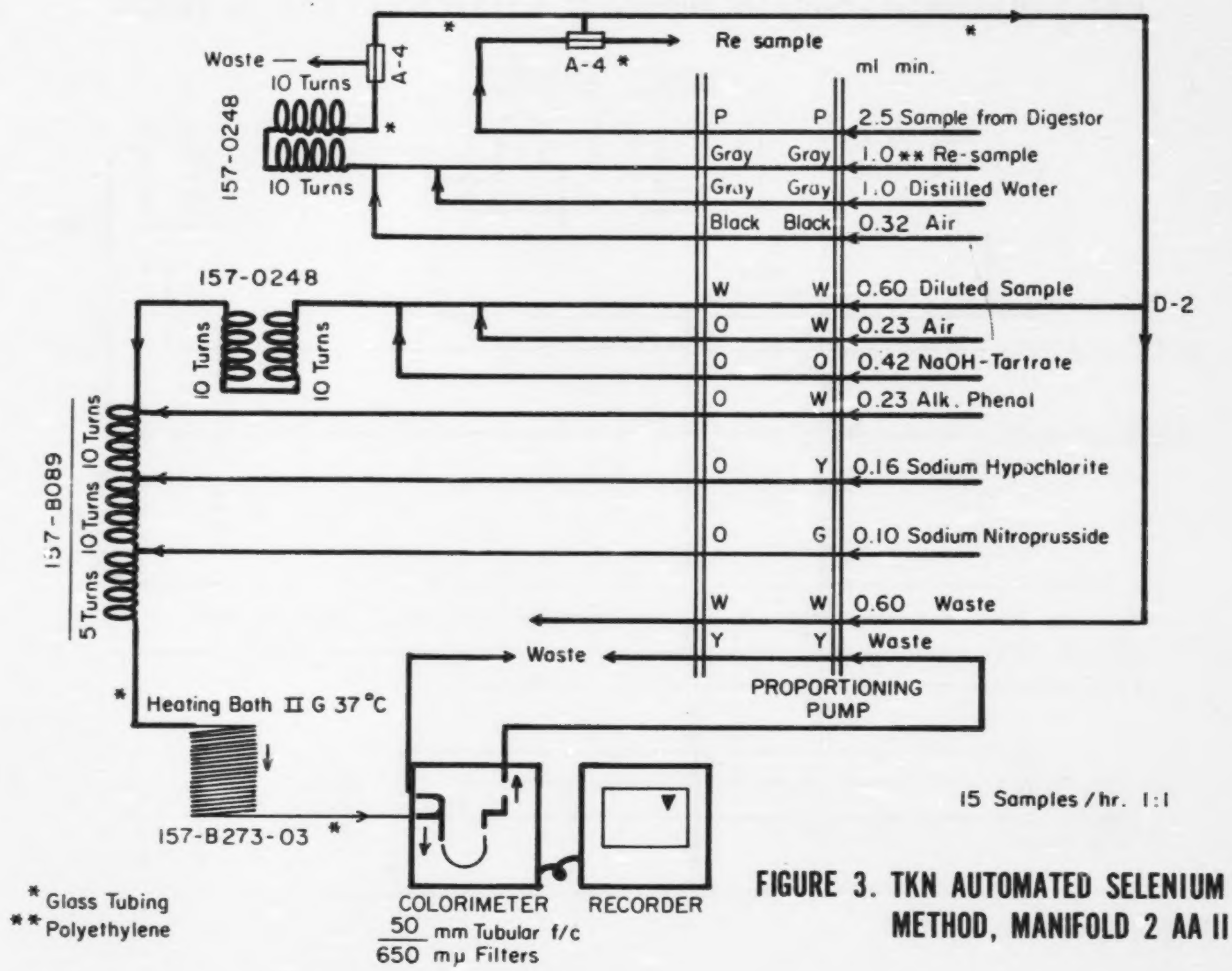

Waste
10 Turns
A-4
157-0248
10 Turns
*
A-4 *
Re sample
ml min.
P P 2.5 Sample from Digestor
Gray Gray 1.0** Re-sample
Gray Gray 1.0 Distilled Water
Black Black 0.32 Air
157-0248
10 Turns
10 Turns
W W 0.60 Diluted Sample
D-2
O W 0.23 Air
O O 0.42 NaOH-Tartrate
O W 0.23 Alk. Phenol
O Y 0.16 Sodium Hypochlorite
O G 0.10 Sodium Nitroprusside
W W 0.60 Waste
Y Y Waste
Waste
157-B089
5 Turns 10 Turns 10 Turns
PROPORTIONING PUMP
* Heating Bath II G 37 °C
157-B273-03 *
15 Samples / hr. 1:1
COLORIMETER
50 mm Tubular f/c
650 mμ Filters
RECORDER
* Glass Tubing
** Polyethylene

FIGURE 3. TKN AUTOMATED SELENIUM METHOD, MANIFOLD 2 AA II

NITROGEN, NITRATE

(Brucine)

STORET NO. 00620

1. Scope and Application

   1.1 This method is applicable to the analysis of drinking, surface, and saline waters, domestic and industrial wastes. Modification can be made to remove or correct for turbidity, color, salinity, or dissolved organic compounds in the sample.

   1.2 The applicable range of concentrations is 0.1 to 2 mg NO_3–N/liter.

2. Summary of Method

   2.1 This method is based upon the reaction of the nitrate ion with brucine sulfate in a 13 N H_2SO_4 solution at a temperature of 100°C. The color of the resulting complex is measured at 410 nm. Temperature control of the color reaction is extremely critical.

3. Sample Handling and Preservation

   3.1 Samples may be preserved by addition of 2 ml conc. H_2SO_4/liter or by addition of 40 mg $HgCl_2$ per liter and storage at 4°C.

4. Interferences

   4.1 Dissolved organic matter will cause an off color in 13 N H_2SO_4 and must be compensated for by additions of all reagents except the brucine-sulfanilic acid reagent. This also applies to natural color present not due to dissolved organics.

   4.2 The effect of salinity is eliminated by addition of sodium chloride to the blanks, standards and samples.

   4.3 All strong oxidizing or reducing agents interfere. The presence of oxidizing agents may be determined by the addition of orthotolidine reagent.

   4.4 Residual chlorine interference is eliminated by the addition of sodium arsenite.

   4.5 Ferrous and ferric iron and quadrivalent manganese give slight positive interferences, but in concentrations less than 1 mg/l these are negligible.

   4.6 Uneven heating of the samples and standards during the reaction time will result in erratic values. The necessity for *absolute control* of temperature during the critical color development period cannot be too strongly emphasized.

5. Apparatus

   5.1 Spectrophotometer or filter photometer suitable for measuring optical densities at 410 nm.

5.2 Sufficient number of 40-50 ml glass sample tubes for reagent blanks, standards, and samples.

5.3 Neoprene coated wire racks to hold sample tubes.

5.4 Water bath suitable for use at 100°C. This bath should contain a stirring mechanism so that all tubes are at the same temperature and should be of sufficient capacity to accept the required number of tubes without significant drop in temperature when the tubes are immersed.

5.5 Water bath suitable for use at 10-15°C.

6. Reagents

6.1 Distilled water free of nitrite and nitrate is to be used in preparation of all reagents and standards.

6.2 Sodium chloride solution (300 g/l): Dissolve 300 g NaCl in distilled water and dilute to 1 liter.

6.3 Sulfuric acid solution: Carefully add 500 ml conc. H_2SO_4 to 125 ml distilled water. Cool and keep tightly stoppered to prevent absorption of atmospheric moisture.

6.4 Brucine-sulfanilic acid reagent: Dissolve 1 g brucine sulfate $[(C_{23}H_{26}N_2O_4)_2 \cdot H_2SO_4 \cdot 7H_2O]$ and 0.1 g sulfanilic acid $(NH_2C_6H_4SO_3H \cdot H_2O)$ in 70 ml hot distilled water. Add 3 ml conc. HCl, cool, mix and dilute to 100 ml with distilled water. Store in a dark bottle at 5°C. This solution is stable for several months; the pink color that develops slowly does not effect its usefulness. *Mark bottle with warning; CAUTION: Brucine Sulfate is toxic; take care to avoid ingestion.*

6.5 Potassium nitrate stock solution: 1.0 ml = 0.1 mg NO_3–N. Dissolve 0.7218 g anhydrous potassium nitrate (KNO_3) in distilled water and dilute to 1 liter in a volumetric flask. Preserve with 2 ml chloroform per liter. This solution is stable for at least 6 months.

6.6 Potassium nitrate standard solution: 1.0 ml = 0.001 mg NO_3–N. Dilute 10.0 ml of the stock solution (6.5) to 1 liter in a volumetric flask. This standard solution should be prepared fresh weekly.

6.7 Acetic acid (1 + 3): Dilute 1 volume glacial acetic acid (CH_3COOH) with 3 volumes of distilled water.

6.8 Sodium hydroxide: Dissolve 40 g of NaOH in distilled water. Cool and dilute to 1 liter.

7. Procedure

7.1 Adjust the pH of the samples to approximately 7 with acetic acid (6.7) or sodium hydroxide (6.8). If necessary, filter to remove turbidity.

7.2 Set up the required number of sample tubes in the rack to handle reagent blank, standards and samples. Space tubes evenly throughout the rack to allow for even flow of bath water between the tubes. This should assist in achieving uniform heating of all tubes.

7.3 If it is necessary to correct for color or dissolved organic matter which will cause color on heating, a set of duplicate samples must be run to which all reagents except the brucine-sulfanilic acid have been added.

7.4 Pipette 10.0 ml of standards and samples or an aliquot of the samples diluted to 10.0 ml into the sample tubes.

7.5 If the samples are saline, add 2 ml of the 30% sodium chloride solution (6.2) to the reagent blank, standards and samples. For fresh water samples, sodium chloride solution may be omitted. Mix contents of tubes by swirling and place rack in cold water bath (0-10°C).

7.6 Pipette 10.0 ml of sulfuric acid solution (6.3) into each tube and mix by swirling. Allow tubes to come to thermal equilibrium in the cold bath. Be sure that temperatures have equilibrated in all tubes before continuing.

7.7 Add 0.5 ml brucine-sulfanilic acid reagent (6.4) to each tube (except the interference control tubes, 7.3) and carefully mix by swirling, then place the rack of tubes in the 100°C water bath for exactly 25 minutes.

Caution: Immersion of the tube rack into the bath should not decrease the temperature of the bath more than 1 to 2°C. In order to keep this temperature decrease to an absolute minimum, flow of bath water between the tubes should not be restricted by crowding too many tubes into the rack. If color development in the standards reveals discrepancies in the procedure, the operator should repeat the procedure after reviewing the temperature control steps.

7.8 Remove rack of tubes from the hot water bath and immerse in the cold water bath and allow to reach thermal equilibrium (20-25°C).

7.9 Read absorbance against the reagent blank at 410 nm using a 1 cm or longer cell.

8. Calculation

8.1 Obtain a standard curve by plotting the absorbance of standards run by the above procedure against mg NO_3–N/l. (The color reaction does not always follow Beer's law).

8.2 Subtract the absorbance of the sample without the brucine-sulfanilic reagent from the absorbance of the sample containing brucine-sulfanilic acid and determine mg

NO_3-N/l. Multiply by an appropriate dilution factor if less than 10 ml of sample is taken.

9. Precision and Accuracy

9.1 Twenty-seven analysts in fifteen laboratories analyzed natural water samples containing exact increments of inorganic nitrate, with the following results:

Increment as Nitrogen, Nitrate mg N/liter	Precision as Standard Deviation mg N/liter	Accuracy as	
		Bias, %	Bias, mg N/liter
0.16	0.092	–6.79	–0.01
0.19	0.083	+8.30	+0.02
1.08	0.245	+4.12	+0.04
1.24	0.214	+2.82	+0.04

(FWPCA Method Study 2, Nutrient Analyses).

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1. Standard Methods for the Examination of Water and Wastewater, 13th Edition, p 461, Method 213-C, (1971).
2. ASTM Standards, Part 23, Water; Atmospheric Analysis, D 992-71, p 363, (1973).
3. Jenkins, D., and Medsken, L., "A Brucine Method for the Determination of Nitrate in Ocean, Estuarine, and Fresh Waters", Anal Chem., *36*, p 610, (1964).

NITROGEN, NITRATE-NITRITE

(Cadmium Reduction Method)

STORET NO. 00630

1. Scope and Application

   1.1 This method pertains to the determination of nitrite singly, or nitrite and nitrate combined in drinking, surface, and saline waters, domestic and industrial wastes. The applicable range of this method is 0.01 to 1.0 mg/l nitrate-nitrite nitrogen. The range may be extended with sample dilution.

2. Summary of Method

   2.1 A filtered sample is passed through a column containing granulated copper-cadmium to reduce nitrate to nitrite. The nitrite (that originally present plus reduced nitrate) is determined by diazotizing with sulfanilamide and coupling with N–(1-naphthyl)–ethylenediamine dihydrochloride to form a highly colored azo dye which is measured spectrophotometrically. Separate, rather than combined nitrate-nitrite values, are readily obtained by carrying out the procedure first with, and then without, the initial Cu-Cd reduction step.

3. Sample Handling and Preservation

   3.1 Analysis should be made as soon as possible. If analysis can be made within 24 hours, the sample should be preserved by refrigeration at 4°C. When samples must be stored for more than 24 hours, they should be preserved with sulfuric acid (2 ml H_2SO_4 per liter) and refrigeration.

   Caution: Samples for reduction column must not be preserved with mercuric chloride.

4. Interferences

   4.1 Build up of suspended matter in the reduction column will restrict sample flow. Since nitrate-nitrogen is found in a soluble state, the sample may be pre-filtered through a glass fiber filter or a 0.45μ membrane filter. Highly turbid samples may be pretreated with zinc sulfate before filtration to remove the bulk of particulate matter present in the sample.

   4.2 Low results might be obtained for samples that contain high concentrations of iron, copper or other metals. EDTA is added to the samples to eliminate this interference.

   4.3 Samples that contain large concentrations of oil and grease will coat the surface of the cadmium. This interference is eliminated by pre-extracting the sample with an organic solvent.

4.4 This procedure determines both nitrate and nitrite. If only nitrate is desired, a separate determination must be made for nitrite and subsequent corrections made. The nitrite may be determined by the procedure below without the reduction step.

5. Apparatus

5.1 Reduction column: The column in Figure I was constructed from a 100 ml pipet by removing the top portion. This column may also be constructed from two pieces of tubing joined end to end. A 10 cm length of 3 cm I.D. tubing is joined to a 25 cm length of 3.5 mm I.D. tubing.

5.2 Spectrophotometer for use at 540 nm, providing a light path of 1 cm or longer.

6. Reagents

6.1 Granulated cadmium: 40-60 mesh (E M Laboratories, Inc., 500 Exec. Blvd., Elmsford, NY 10523, Cat. 2001 Cadmium, Coarse Powder).

6.2 Copper-Cadmium: The cadmium granules (new or used) are cleaned with dilute HCl and copperized with 2% solution of copper sulfate in the following manner:

6.2.1 Wash the cadmium with dilute HCl (6.10) and rinse with distilled water.

6.2.2 Swirl 25 g cadmium in 100 ml portions of a 2% solution of copper sulfate (6.11) for 5 minutes or until blue color partially fades, decant and repeat with fresh copper sulfate until a brown colloidal precipitate forms.

6.2.3 Wash the copper-cadmium with distilled water (at least 10 times) to remove all the precipitated copper.

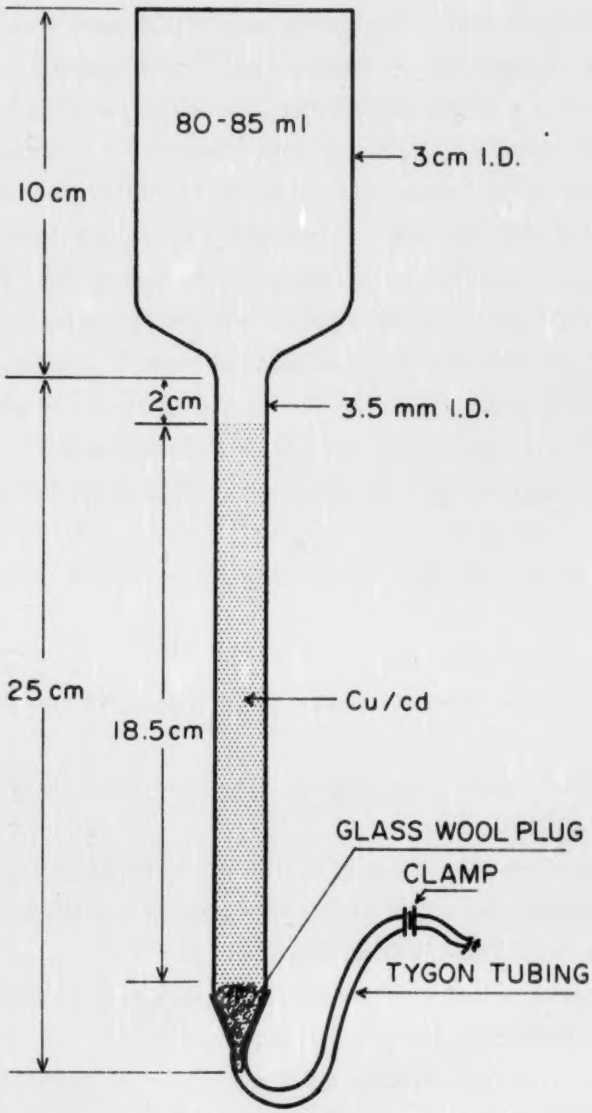
80-85 ml
3cm I.D.
10cm
2cm
3.5 mm I.D.
25cm
18.5cm
Cu/cd
GLASS WOOL PLUG
CLAMP
TYGON TUBING

FIGURE 1. REDUCTION COLUMN

6.3 Preparation of reaction column: Insert a glass wool plug into the bottom of the reduction column and fill with distilled water. Add sufficient copper-cadmium granules to produce a column 18.5 cm in length. Maintain a level of distilled water above the copper-cadmium granules to eliminate entrapment of air. Wash the column with 200 ml of dilute ammonium chloride solution (6.5). The column is then activated by passing through the column 100 ml of a solution composed of 25 ml of a 1.0 mg/l NO_3–N standard and 75 ml of ammonium chloride – EDTA solution (6.4). Use a flow rate between 7 and 10 ml per minute.

6.4 Ammonium chloride – EDTA solution: Dissolve 13 g ammonium chloride and 1.7 g disodium ethylenediamine tetracetate in 900 ml of distilled water. Adjust the pH to 8.5 with conc. ammonium hydroxide (6.9) and dilute to 1 liter.

6.5 Dilute ammonium chloride-EDTA solution: Dilute 300 ml of ammonium chloride-EDTA solution (6.4) to 500 ml with distilled water.

6.6 Color reagent: Dissolve 10 g sulfanilamide and 1 g N(1-naphthyl)–ethylenediamine dihydrochloride in a mixture of 100 ml conc. phosphoric acid and 800 ml of distilled water and dilute to 1 liter with distilled water.

6.7 Zinc sulfate solution: Dissolve 100 g $ZnSO_4 \cdot 7H_2O$ in distilled water and dilute to 1 liter.

6.8 Sodium hydroxide solution, 6N: Dissolve 240 g NaOH in 500 ml distilled water, cool and dilute to 1 liter.

6.9 Ammonium hydroxide, conc.

6.10 Dilute hydrochloric acid, 6N: Dilute 50 ml of conc. HCl to 100 ml with distilled water.

6.11 Copper sulfate solution, 2%: Dissolve 20 g of $CuSO_4 \cdot 5H_2O$ in 500 ml of distilled water and dilute to 1 liter.

6.12 Stock nitrate solution: Dissolve 7.218 g KNO_3 in distilled water and dilute to 1000 ml. Preserve with 2 ml of chloroform per liter. This solution is stable for at least 6 months. 1.0 ml = 1.00 mg NO_3–N.

6.13 Standard nitrate solution: Dilute 10.0 ml of nitrate stock solution (6.12) to 1000 ml with distilled water. 1.0 ml = 0.01 mg NO_3–N.

6.14 Stock nitrite solution: Dissolve 6.072 g KNO_2 in 500 ml of distilled water and dilute to 1000 ml. Preserve with 2 ml of chloroform and keep under refrigeration. Stable for approximately 3 months. 1.0 ml = 1.00 mg NO_2–N.

6.15 Standard nitrite solution: Dilute 10.0 ml of stock nitrite solution (6.14) to 1000 ml with distilled water. 1.0 ml = 0.01 mg NO_2–N.

6.16 Using standard nitrate solution (6.13) prepare the following standards in 100 ml volumetric flasks:

Conc., mg-NO_3–N/l	ml of Standard Solution/100.0 ml
0.00	0.0
0.05	0.5
0.10	1.0
0.20	2.0
0.50	5.0
1.00	10.0

7. Procedure

7.1 Turbidity removal: One of the following methods may be used to remove suspended matter.

7.1.1 Filter sample through a glass fiber filter or a 0.45μ membrane filter.

7.1.2 Add 1 ml zinc sulfate solution (6.7) to 100 ml of sample and mix thoroughly. Add 0.4-0.5 ml sodium hydroxide solution (6.8) to obtain a pH of 10.5 as determined with a pH meter. Let the treated sample stand a few minutes to allow the heavy flocculent precipitate to settle. Clarify by filtering through a glass fiber filter or a 0.45μ membrane filter.

7.2 Oil and grease removal: Adjust the pH of 100 ml of filtered sample to 2 by addition of conc. HCl. Extract the oil and grease from the aqueous solution with two 25 ml portions of a non-polar solvent (Freon, chloroform or equivalent).

7.3 If the pH of the sample is below 5 or above 9, adjust to between 5 and 9 with either conc. HCl or conc. NH_4OH. This is done to insure a sample pH of 8.5 after step (7.4).

7.4 To 25.0 ml of sample or an aliquot diluted to 25.0 ml, add 75 ml of ammonium chloride-EDTA solution (6.4) and mix.

7.5 Pour sample into column and collect sample at a rate of 7-10 ml per minute.

7.6 Discard the first 25 ml, collect the rest of the sample (approximately 70 ml) in the original sample flask.

7.7 Add 2.0 ml of color reagent (6.6) to 50.0 ml of sample. Allow 10 minutes for color development. Within 2 hours measure the absorbance at 540 nm against a reagent blank.

NOTE: If the concentration of sample exceeds 1.0 mg NO_3–N/l, the remainder of the reduced sample may be used to make an appropriate dilution before proceeding with step (7.7).

7.8 Standards: Carry out the reduction of standards exactly as described for the samples. At least one nitrite standard should be compared to a reduced nitrate standard at the same concentration to verify the efficiency of the reduction column.

8. Calculation

8.1 Obtain a standard curve by plotting the absorbance of standards run by the above procedure against NO_3-N mg/l. Compute concentration of samples by comparing sample absorbance with standard curve.

8.2 If less than 25 ml of sample is used for the analysis the following equation should be used:

$$\text{mg } NO_2 + NO_3-N/l = \frac{A \times 25}{\text{ml sample used}}$$

where:

A = Concentration of nitrate from standard curve.

9. Precision and Accuracy

9.1 In a single laboratory (MDQARL), using sewage samples at concentrations of 0.04, 0.24, 0.55 and 1.04 mg $NO_3 + NO_2-N/l$, the standard deviations were ±0.005, ±0.004, ±0.005 and ±0.01, respectively.

9.2 In a single laboratory (MDQARL), using sewage samples at concentrations of 0.24, 0.55, and 1.05 mg $NO_3 + NO_2-N/l$, the recoveries were 100%, 102% and 100%, respectively.

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NITROGEN, NITRATE-NITRITE

(Automated Cadmium Reduction Method)

STORET NO. 00630

1. Scope and Application

1.1 This method pertains to the determination of nitrite singly, or nitrite and nitrate combined in surface and saline waters, and domestic and industrial wastes. The applicable range of this method is 0.05 to 10.0 mg/l nitrate-nitrite nitrogen. The range may be extended with sample dilution.

2. Summary of Method

2.1 A filtered sample is passed through a column containing granulated copper-cadmium to reduce nitrate to nitrite. The nitrite (that originally present plus reduced nitrate) is determined by diazotizing with sulfanilamide and coupling with N–(1-napthyl)–ethylenediamine dihydrochloride to form a highly colored azo dye which is measured colorimetrically. Separate, rather than combined nitrate-nitrite values, are readily obtained by carrying out the procedure first with, and then without, the initial Cu-Cd reduction step.

3. Sample Handling and Preservation

3.1 Analysis should be made as soon as possible. If analysis can be made within 24 hours, the sample should be preserved by refrigeration at 4°C. When samples must be stored for more than 24 hours, they should be preserved with sulfuric acid (2 ml conc. H_2SO_4 per liter) and refrigeration.

Caution: Samples for reduction column must not be preserved with mercuric chloride.

4. Interferences

4.1 Sample turbidity and color may interfere with this method. Turbidity must be removed by filtration prior to analysis. Sample color that absorbs in the photometric range used for analysis will also interfere.

5. Apparatus

5.1 Technicon AutoAnalyzer (AAI or AAII) consisting of the following components:

- 5.1.1 Sampler.
- 5.1.2 Manifold (AAI) or analytical cartridge (AAII).
- 5.1.3 Colorimeter equipped with a 15 mm or 50 mm tubular flow cell and 540 nm filters.
- 5.1.4 Recorder.

5.1.5 Digital printer for AAII (Optional).

6. Reagents

6.1 Granulated cadmium: 40-60 mesh (E M Laboratories, Inc., 500 Exec. Blvd., Elmsford, NY 10523, Cat. 2001 Cadmium, Coarse Powder).

6.2 Copper-cadmium: The cadmium granules (new or used) are cleaned with dilute HCl (6.7) and copperized with 2% solution of copper sulfate (6.8) in the following manner:

6.2.1 Wash the cadmium with HCl (6.7) and rinse with distilled water.

6.2.2 Swirl 10 g cadmium in 100 ml portions of 2% solution of copper sulfate (6.8) for five minutes or until blue color partially fades, decant and repeat with fresh copper sulfate until a brown colloidal precipitate forms.

6.2.3 Wash the cadmium-copper with distilled water (at least 10 times) to remove all the precipitated copper.

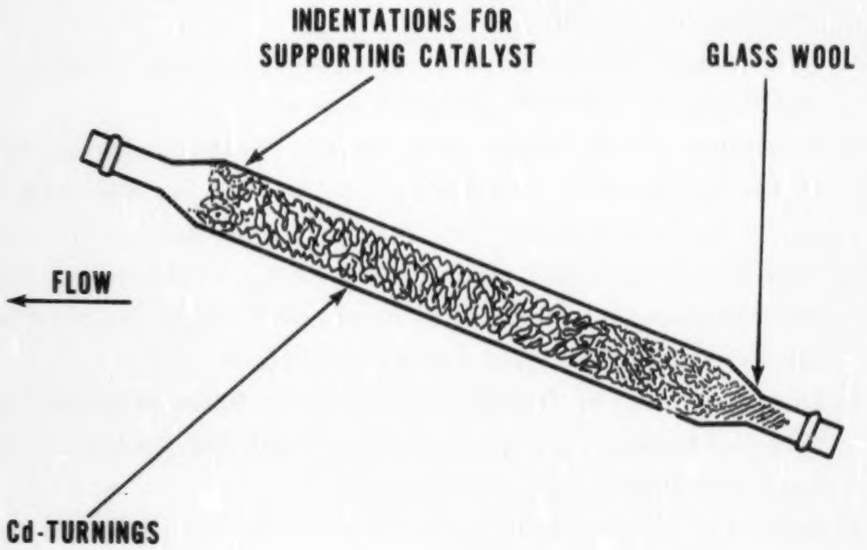
6.3 Preparation of reduction column AAI: The reduction column is an 8 by 50 mm glass tube with the ends reduced in diameter to permit insertion into the system. Copper-cadmium granules (6.2) are placed in the column between glass wool plugs. The packed reduction column is placed in an up-flow 20° incline to minimize channeling. See Figure 1.

6.4 Preparation of reduction column AAII: The reduction column is a U-shaped, 35 cm length, of 2 mm I.D. glass tubing (Note 1). Fill the reduction column with distilled water to prevent entrapment of air bubbles during the filling operations. Transfer the copper-cadmium granules (6.2) to the reduction column and place a glass wool plug in each end. To prevent entrapment of air bubbles in the reduction column be sure that all pump tubes are filled with reagents before putting the column into the analytical system.

NOTE 1: A 0.081 I.D. pump tube (purple) can be used in place of the 2 mm glass tube.

6.5 Distilled water: Because of possible contamination, this should be prepared by passage through an ion exchange column comprised of a mixture of both strongly acidic-cation and strongly basic-anion exchange resins. The regeneration of the ion exchange column should be carried out according to the manufacturer's instructions.

6.6 Color reagent: To approximately 800 ml of distilled water, add, while stirring, 100 ml conc. phosphoric acid, 40 g sulfanilamide, and 2 g N-l naphthylethylenediamine dihydrochloride. Stir until dissolved and dilute to 1 liter. Store in brown


INDENTATIONS FOR SUPPORTING CATALYST
GLASS WOOL
FLOW
Cd-TURNINGS

TILT COLUMN TO 20° POSTION

FIGURE 1. COPPER-CADMIUM REDUCTION COLUMN
(1 1/2 ACTUAL SIZE)

bottle and keep in the dark when not in use. This solution is stable for several months.

6.7 Dilute hydrochloric acid, 6N: Dilute 50 ml of conc. HCl to 100 ml with distilled water.

6.8 Copper sulfate solution, 2%: Dissolve 20 g of $CuSO_4 \cdot 5H_2O$ in 500 ml of distilled water and dilute to 1 liter.

6.9 Wash solution: Use distilled water for unpreserved samples; samples preserved with H_2SO_4, use 2 ml H_2SO_4 per liter of wash water.

6.10 Ammonium chloride solution (8.5% NH_4Cl): Dissolve 85 g of reagent grade ammonium chloride in distilled water and dilute to 1 liter with distilled water. Add 1/2 ml Brij-35 (Available from Technicon Corporation).

6.11 Stock nitrate solution: Dissolve 7.218 g KNO_3 and dilute to 1 liter in a volumetric flask with distilled water. Preserve with 2 ml of chloroform per liter. Solution is stable for 6 months. 1 ml = 1.0 mg NO_3–N.

6.12 Stock nitrite solution: Dissolve 6.072 g KNO_2 in 500 ml of distilled water and dilute to 1 liter in a volumetric flask. Preserve with 2 ml of chloroform and keep under refrigeration. 1.0 ml = 1.0 mg NO_2–N.

6.13 Standard nitrate solution: Dilute 10.0 ml of stock nitrate solution (6.11) to 1000 ml. 1.0 ml = 0.01 mg NO_3–N. Preserve with 2 ml of chloroform per liter. Solution is stable for 6 months.

6.14 Standard nitrite solution: Dilute 10.0 ml of stock nitrite (6.12) solution to 1000 ml. 1.0 ml = 0.01 mg NO_2–N. Solution is unstable; prepare as required.

6.15 Using standard nitrate solution (6.13), prepare the following standards in 100.0 ml volumetric flasks. At least one nitrite standard should be compared to a nitrate standard at the same concentration to verify the efficiency of the reduction column.

Conc., mg NO_2–N or NO_3–N/l	ml Standard Solution/100 ml
0.0	0
0.05	0.5
0.10	1.0
0.20	2.0
0.50	5.0
1.00	10.0
2.00	20.0
4.00	40.0
6.00	60.0

NOTE 2: When the samples to be analyzed are saline waters, Substitute Ocean Water (SOW) should be used for preparing the standards; otherwise, distilled water is used. A tabulation of SOW composition follows:

NaCl – 24.53 g/l
$CaCl_2$ – 1.16 g/l
KBr – 0.10 g/l
NaF – 0.003 g/l
$MgCl_2$ – 5.20 g/l
KCL – 0.70 g/l
H_3BO_3 – 0.03 g/l
Na_2SO_4 – 4.09 g/l
$NaHCO_3$ – 0.20 g/l
$SrCl_2$ – 0.03 g/l

7. Procedure

7.1 If the pH of the sample is below 5 or above 9, adjust to between 5 and 9 with either conc. HCl or conc. NH_4OH.

7.2 Set up the manifold as shown in Figure 1 (AAI) or Figure 2 (AAII). Note that reductant column should be in 20° incline position (AAI). Care should be taken not to introduce air into reduction column on the AAII.

7.3 Allow both colorimeter and recorder to warm up for 30 minutes. Obtain a stable baseline with all reagents, feeding distilled water through the sample line.

7.4 Place appropriate nitrate and/or nitrite standards in sampler in order of decreasing concentration of nitrogen. Complete loading of sampler tray with unknown samples.

7.5 For the AAI system, sample at a rate of 30/hr, 1:1. For the AAII, use a 40/hr, 4:1 cam and a common wash.

7.6 Switch sample line to sampler and start analysis.

8. Calculations

8.1 Prepare appropriate standard curve or curves derived from processing NO_2 and/or NO_3 standards through manifold. Compute concentration of samples by comparing sample peak heights with standard curve.

9. Precision and Accuracy

9.1 Three laboratories analyzed four natural water samples containing exact increments of inorganic nitrate, with the following results:

Increment as Nitrate Nitrogen mg N/liter	Precision as Standard Deviation mg N/liter	Accuracy as Bias, %	Accuracy as Bias, mg N/liter
0.29	0.012	+ 5.75	+0.017
0.35	0.092	+18.10	+0.063
2.31	0.318	+ 4.47	+0.103
2.48	0.176	– 2.69	–0.067

(FWQA Method Study 4, Automated Methods – In preparation)

Bibliography

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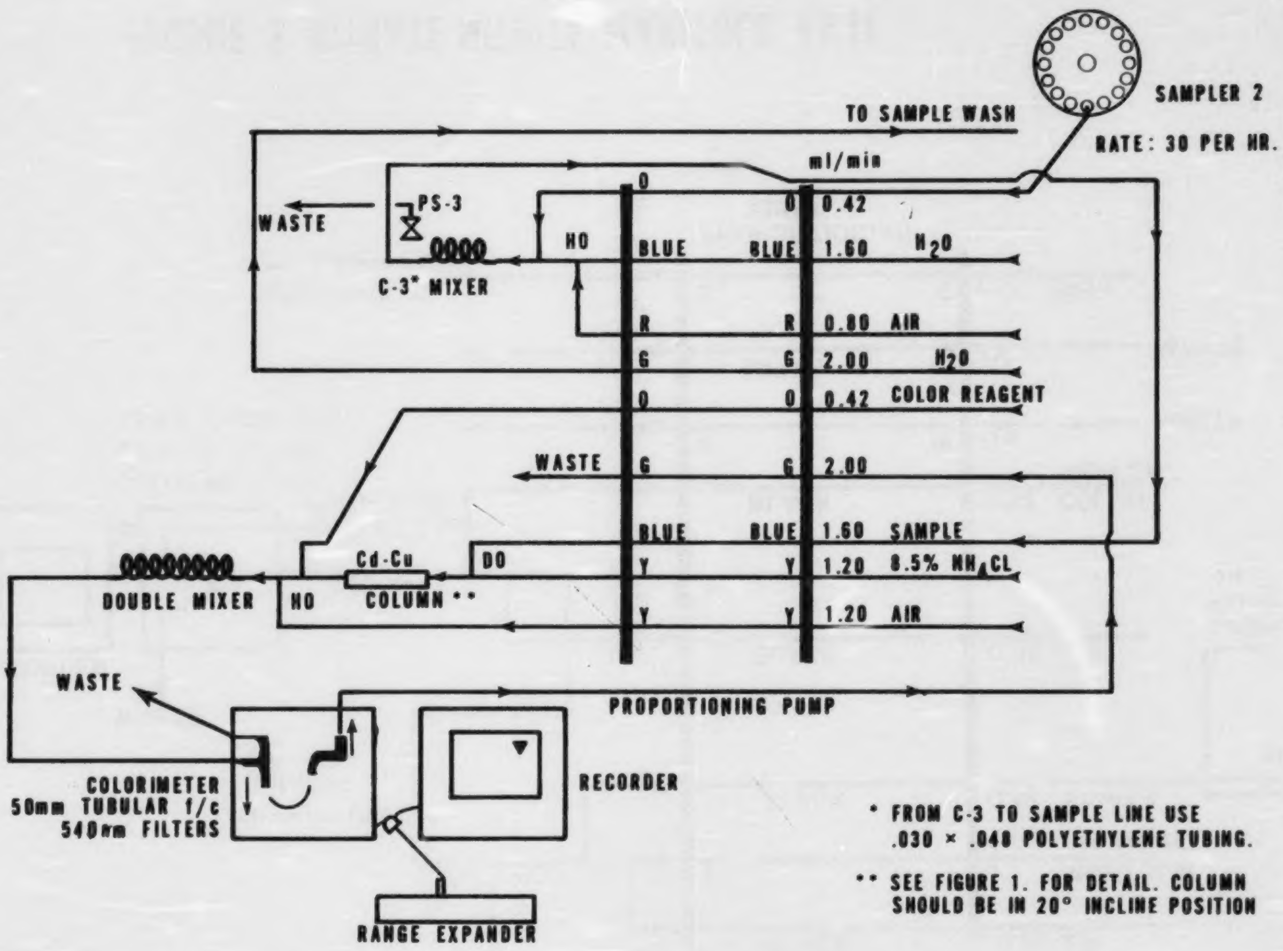
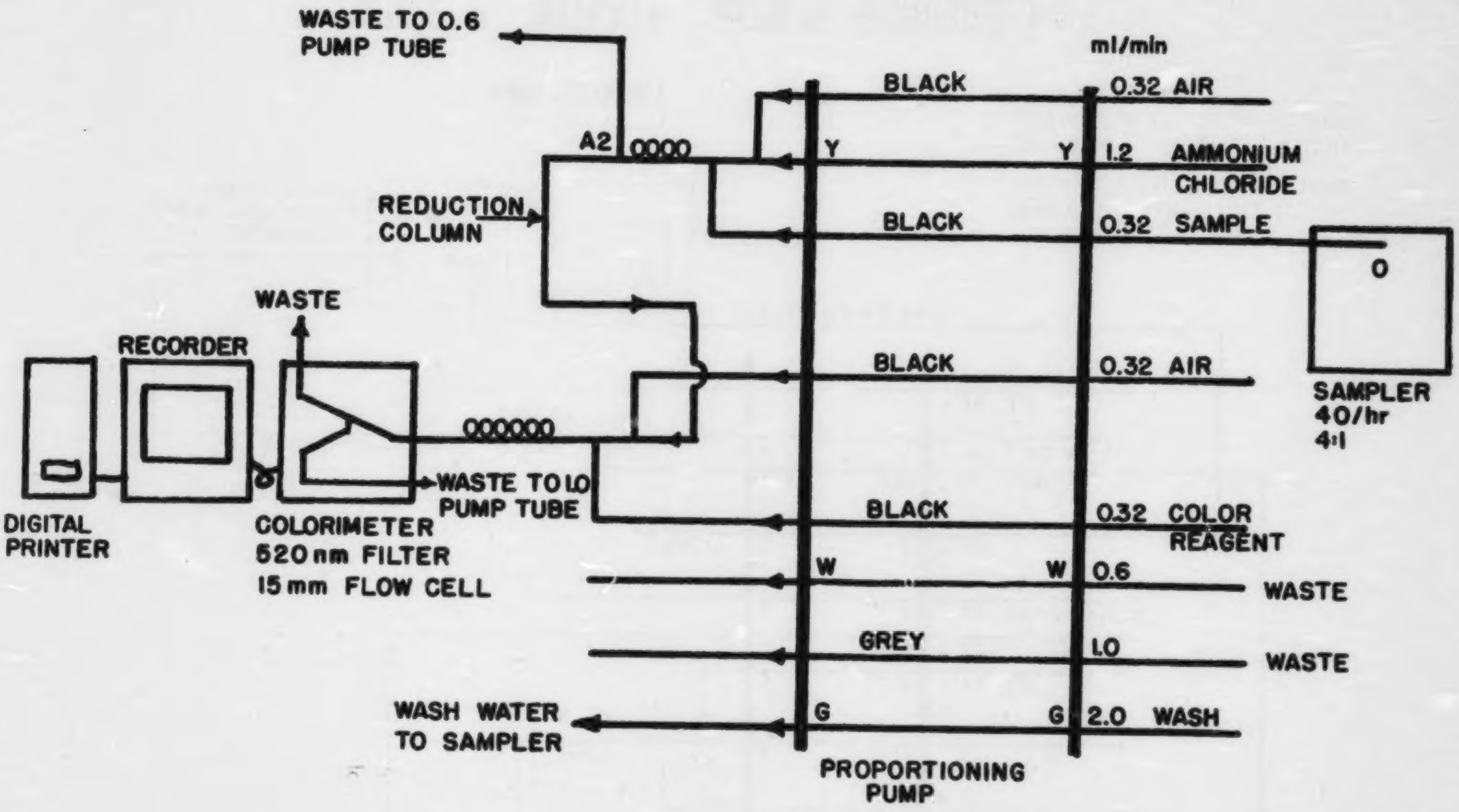

SAMPLER 2
RATE: 30 PER HR.
TO SAMPLE WASH
ml/min
WASTE
PS-3
C-3* MIXER
HO
O
BLUE
R
G
O
G
BLUE
Y
Y
O 0.42
BLUE 1.60 H_2O
R 0.80 AIR
G 2.00 H_2O
O 0.42 COLOR REAGENT
WASTE
G 2.00
BLUE 1.60 SAMPLE
Y 1.20 8.5% NH_4CL
Y 1.20 AIR
Cd-Cu
COLUMN **
DO
HO
DOUBLE MIXER
WASTE
PROPORTIONING PUMP
COLORIMETER
50mm TUBULAR f/c
540nm FILTERS
RECORDER
RANGE EXPANDER

* FROM C-3 TO SAMPLE LINE USE .030 × .040 POLYETHYLENE TUBING.

** SEE FIGURE 1. FOR DETAIL. COLUMN SHOULD BE IN 20° INCLINE POSITION

FIGURE 2. NITRATE - NITRITE MANIFOLD AA-I



WASTE TO 0.6
PUMP TUBE
ml/min
BLACK
0.32 AIR
A2
0000
Y
Y
1.2
AMMONIUM
CHLORIDE
REDUCTION
COLUMN
BLACK
0.32
SAMPLE
O
WASTE
RECORDER
BLACK
0.32 AIR
SAMPLER
40/hr
4:1
0000000
WASTE TO 1.0
PUMP TUBE
BLACK
0.32
COLOR
REAGENT
DIGITAL
PRINTER
COLORIMETER
520 nm FILTER
15 mm FLOW CELL
W
W
0.6
WASTE
GREY
1.0
WASTE
WASH WATER
TO SAMPLER
G
G
2.0
WASH
PROPORTIONING
PUMP

FIGURE 3 NITRATE-NITRITE MANIFOLD AA II

NITROGEN, NITRITE

STORET NO. 00615

1. Scope and Application

   1.1 This method is applicable to the determination of nitrite in drinking, surface, and saline waters, domestic and industrial wastes.

   1.2 The method is applicable in the range from 0.01 to 1.0 mg NO_2–N/l.

2. Summary of Method

   2.1 The diazonium compound formed by diazotation of sulfanilamide by nitrite in water under acid conditions is coupled with N–(1-naphthyl)–ethylenediamine to produce a reddish-purple color which is read in a spectrophotometer at 540 nm.

3. Sample Handling and Preservation

   3.1 Samples should be analyzed as soon as possible. They may be stored for 24 to 48 hours at 4°C.

4. Interferences

   4.1 There are very few known interferences at concentrations less than 1,000 times that of the nitrite; however, the presence of strong oxidants or reductants to the samples will readily affect the nitrite concentrations. High alkalinity (>600 mg/l) will give low results due to a shift in pH.

5. Apparatus

   5.1 Spectrophotometer equipped with 1 cm or larger cells for use at 540 nm.

   5.2 Nessler tubes, 50 ml or volumetric flasks, 50 ml.

6. Reagents

   6.1 Distilled water free of nitrite and nitrate is to be used in preparation of all reagents and standards.

   6.2 Buffer-color reagent: To 250 ml of distilled water, add 105 ml conc. hydrochloric acid, 5.0 g sulfanilamide and 0.5 g N–(1-naphthyl) ethylenediamine dihydrochloride. Stir until dissolved. Add 136 g of sodium acetate ($CH_3COONa \cdot 3H_2O$) and again stir until dissolved. Dilute to 500 ml with distilled water. This solution is stable for several weeks if stored in the dark.

   6.3 Nitrite stock solution: 1.0 ml = 0.10 mg NO_2–N. Dissolve 0.4926 g of dried anhydrous sodium nitrite (24 hours in desiccator) in distilled water and dilute to 1000 ml. Preserve with 2 ml chloroform per liter.

   6.4 Nitrite standard solution: 1.0 ml = 0.001 mg NO_2–N. Dilute 10.0 ml of the stock solution (6.3) to 1000 ml.

7. Procedure

7.1 If the sample has a pH greater than 10 or a total alkalinity in excess of 600 mg/l, adjust to approximately pH 6 with 1:3 HCl.

7.2 If necessary, filter the sample through a 0.45 μ pore size filter using the first portion of filtrate to rinse the filter flask.

7.3 Place 50 ml of sample, or an aliquot diluted to 50 ml, in 50 ml Nessler tube; hold until preparation of standards is completed.

7.4 At the same time prepare a series of standards in 50 ml Nessler tubes as follows:

ml of Standard Solution 1.0 ml = 0.001 mg NO_2-N	Conc., When Diluted to 50 ml, mg/l of NO_2-N
0.0 (Blank)	0.0
0.5	0.01
1.0	0.02
1.5	0.03
2.0	0.04
3.0	0.06
4.0	0.08
5.0	0.10
10.0	0.20

7.5 Add 2 ml of buffer-color reagent (6.2) to each standard and sample, mix and allow color to develop for at least 15 minutes. The color reaction medium should be between pH 1.5 and 2.0.

7.6 Read the color in the spectrophotometer at 540 nm against the blank and plot concentration of NO_2-N against absorbance.

8. Calculation

8.1 Read the concentration of NO_2-N directly from the curve.

8.2 If less than 50.0 ml of sample is taken, calculate mg/l as follows:

$$NO_2-N, \text{ mg/l} = \frac{\text{mg/l from standard curve} \times 50}{\text{ml sample used}}$$

9. Precision and Accuracy

9.1 Precision and accuracy data are not available at this time.

NTA

(Zinc-Zincon Method)

STORET NO. 00695

1. Scope and Application

    1.1 In this method, NTA refers to the tri-sodium salt of nitrilotriacetic acid, $N(CH_2COONa)_3$.

    1.2 This method is applicable to surface waters in the range of 0.5–10.0 mg/l NTA.

2. Summary of Method(1)

    2.1 Zinc forms a blue-colored complex with 2 carboxy-2′-hydroxy-5′-sulfoformazylbenzene (Zincon) in a solution buffered to pH 9.2. When NTA is added, the Zn-Zincon complex is broken which reduces the optical density in proportion to the amount of NTA present.

3. Sample Handling and Preservation

    3.1 Samples should be analyzed as soon as possible, as NTA has been shown to be biodegradable(2).

4. Interferences

    4.1 Cations, such as calcium, magnesium, zinc, copper, iron, and manganese, complex with NTA and give a negative interference. These ions are removed by batch treating samples with ion-exchange resin. At concentrations higher than expected in typical river waters(3), only zinc, copper, and iron were not completely removed with ion-exchange treatment. Results are summarized in Table 1.

TABLE 1

Interference of Common Metals

Metal	mg/l added	1.0 mg/l NTA	5.0 mg/l NTA
		Recoveries	
Blank	0.0	1.1	5.5
Zinc	2.0	<0.5	0.6

TABLE 1-(Cont'd)

Metal	mg/l added	1.0 mg/l NTA	5.0 mg/l NTA
		Recoveries	
Boron	5.0	1.1	5.5
Iron	5.0	0.95	4.6
Molybdenum	2.0	1.0	5.5
Manganese	4.0	1.1	5.6
Aluminum	3.0	0.85	5.2
Copper	0.5	<0.5	3.4
Strontium	5.0	1.0	5.4

4.2 This method has not been found applicable to salt waters.

5. Apparatus

5.1 Shaking machine, tray type, for stirring sample-resin mixtures in 125 ml Erlenmeyer flasks.

5.2 Photometer, suitable for measurements at 620 nm.

6. Reagents

6.1 Sodium hydroxide, 6N: Dissolve 120 g NaOH in distilled water and dilute to 500 ml.

6.2 Buffer: Dissolve 31 g boric acid and 37 g potassium chloride in 800 ml distilled water. Adjust pH to 9.2 with 6N NaOH (6.1). Dilute to 1 liter.

6.3 Hydrochloric acid, 2N: Dilute 83 ml conc. HCl to 500 ml with distilled water.

6.4 Zinc: Dissolve 0.44 g $ZnSO_4 \cdot 7H_2O$ in 100 ml 2N HCl (6.3) and dilute to 1 liter with distilled water.

6.5 Sodium hydroxide, 1N: Dissolve 4 g NaOH in distilled water and dilute to 100 ml.

6.6 Zinc-Zincon: Dissolve 0.13 g Zincon (2-carboxy-2′-hydroxy-5′-sulfoformazyl benzene) in 2 ml 1N NaOH (6.5). Add 300 ml buffer (6.2). While stirring, add 15 ml Zinc solution (6.4) and dilute to 1 liter with distilled water.

6.7 Ion-exchange resin: Dowex 50W-X8, 50-100 mesh, Na+ form (or equivalent).

6.8 Stock NTA solution: Dissolve 1.0700 g $N(CH_2COONa)_3 \cdot H_2O$ in distilled water and dilute to 1000 ml. 1.0 ml = 0.01 mg NTA.

7. Procedure

7.1 Filter approximately 50 ml of well-mixed sample through a 0.45μ membrane filter.

7.2 Prepare a series of standards from 0.5 to 10 mg/l NTA, including a blank of distilled water. Treat standards and blank in same manner as filtered samples.

7.3 To a 25 ml sample in a 125 ml Erlenmeyer flask add approximately 2.5 g ion-exchange resin. Agitate sample for at least 15 minutes.

7.4 Filter through coarse filter paper to remove resin. Pipette 15.0 ml of filtrate into a 50 ml beaker. Add 25.0 ml Zinc-Zincon (6.6) by pipette.

7.5 Read absorbance against distilled water at 620 nm in a 1 cm or 2 cm cell.

8. Calculation

8.1 Prepare standard curve by plotting absorbance of standards vs. NTA concentrations. Calculate concentrations of NTA, mg/l, directly from this curve.

9. Precision and Accuracy

9.1 In a single laboratory (MDQARL), using spiked surface water samples at concentrations of 0.5, 2, 6, and 10 mg/l NTA, standard deviations were ±0.17, ±0.14, ±0.1, and ±0.16, respectively.

9.2 In a single laboratory (MDQARL), using spiked surface water samples at concentrations of 1.0 and 7.5 mg/l NTA, recoveries were 120% and 103%, respectively.

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NTA

(Automated Zinc-Zincon Method)

STORET NO. 00695

1. Scope and Application

1.1 In this method, NTA refers to the tri-sodium salt of nitrilotriacetic acid, $N(CH_2COONa)_3$.

1.2 This method is applicable to surface waters in the range of 0.04 to 1.0 mg/l and 0.5 to 10.0 mg/l NTA, depending on which manifold system is used. It does not apply to saline waters; a positive interference of 0.5 to 1.0 mg/l is present in sewage-type samples.

1.3 Approximately 13 samples per hour can be analyzed.

2. Summary of Method(1)

2.1 Zinc forms a blue-colored complex with 2-carboxy-2′-hydroxy-5′-sulfoformazylbenzene (Zincon) in a solution buffered to pH 9.2. When NTA is added, the Zn-Zincon complex is broken which reduces the optical density in proportion to the amount of NTA present.

3. Sample Handling and Preservation

3.1 Samples should be analyzed as soon as possible, as NTA has been shown to be biodegradable.(2)

4. Interferences

4.1 Cations, such as calcium, magnesium, zinc, copper, iron, and manganese, complex with NTA and give a negative interference. These ions are removed automatically by passing the sample through an ion-exchange column. At concentrations higher than expected in typical river waters,(3) only iron was not completely removed by this column treatment. Results, summarized in Tables 1 and 2, show that iron gives a negative interference in concentrations above 3.0 mg/l NTA.

TABLE 1

Interference of Common Metals

Metal	mg/l added	1.0 mg/l NTA	5.0 mg/l NTA
		Recoveries	
Blank	0.0	1.0	5.0
Zinc	2.0	0.9	4.9
Iron	5.0	0.8	3.8
Manganese	4.0	1.0	4.9
Copper	0.5	1.2	4.9

TABLE 2

Effect of Iron on NTA Recovery in River Water

Iron Added mg/l	NTA Recovered, mg/l (0.5 mg/l added)
0.0	0.52
0.5	0.52
1.0	0.52
2.0	0.52
3.0	0.48
4.0	0.45
5.0	0.39

4.2 At concentration levels below 0.05 mg/l NTA, negative peaking may occur during analyses.

5. Apparatus

5.1 Technicon AutoAnalyzer consisting of:

- 5.1.1 Sampler I or II.
- 5.1.2 Manifold.
- 5.1.3 Proportioning pump.

5.1.4 Colorimeter equipped with 15 mm tubular flow cell and 600 or 625 nm filter.

5.1.5 Recorder.

6. Reagents

6.1 Sodium hydroxide, 6N: Dissolve 120 g NaOH in distilled water and dilute to 500 ml.

6.2 Buffer: Dissolve 31 g boric acid and 37 g potassium chloride in 800 ml distilled water. Adjust pH of solution to 9.2 with 6N NaOH (6.1). Dilute to 1 liter.

6.3 Hydrochloric acid, 2N: Dilute 83 ml conc. HCl to 500 ml with distilled water.

6.4 Zinc: Dissolve 0.44 g $ZnSO_4 \cdot 7H_2O$ in 100 ml 2N HCl (6.3). Dilute to 1 liter with distilled water.

6.5 Sodium hydroxide, 1N: Dissolve 4 g NaOH in distilled water and dilute to 100 ml.

6.6 Zinc-Zincon reagent A (0.04-1.0 mg/l NTA): Dissolve 0.065 g Zincon powder (2-carboxy-2′-hydroxy-5′-sulfoformazyl benzene) in 2 ml of 1 N NaOH (6.5). Add 300 ml buffer (6.2). Stir on a magnetic stirrer and add 7.5 ml zinc solution (6.4). Dilute to 1 liter with distilled water. *This solution is stable for 12 hours.*

6.7 Zinc-Zincon reagent B (0.5-10 mg/l NTA): Dissolve 0.13 g Zincon in 2 ml 1N NaOH (6.5). Stir on magnetic stirrer and add 300 ml buffer (6.2) and 15 ml zinc solution (6.4). Dilute to 1 liter with distilled water. *Stable for 1 week.*

6.8 Ion-exchange resin, H^+ form: 20-50 mesh or 30-80 mesh, Dowex 50W-XB or equivalent.

NOTE: Column is prepared by sucking a water slurry of the resin into 12 inches of 3/16-inch OD sleeving. This may be conveniently done by using a pipette and a loose-fitting glass wool plug in the sleeve.

6.9 Stock NTA solution: Dissolve 1.0700 g of $N(CH_2COONa)_3 \cdot H_2O$ in 500 ml of distilled water and dilute to 1000 ml. 1.0 ml = 1.0 mg NTA.

6.10 Working solution A: Dilute 10.0 ml of stock NTA solution to 100.0 ml with distilled water. 1.0 ml = 0.1 mg NTA. Prepare daily.

6.11 Working solution B: Dilute 10.0 ml of Solution A to 100.0 ml with distilled water. 1.0 ml = 0.01 mg NTA. Prepare daily.

6.12 Working solution C: Dilute 10.0 ml of Solution B to 100.0 ml with distilled water. 1.0 ml = 0.001 mg NTA. Prepare daily.

6.13 Prepare a series of standards by diluting suitable volumes of working solutions to 100.0 ml with distilled water. The following dilutions are suggested:

ml of Solution C/100 ml	Conc., mg NTA/1
2	0.02
4	0.04
6	0.06
8	0.08
10	0.10
ml of Solution B/100 ml	
2	0.20
4	0.40
6	0.60
8	0.80
10	1.00
ml of Solution A/100 ml	
2	2.0
4	4.0
6	6.0
8	8.0
10	10.0

7. Procedure

7.1 Set up manifold as shown in Figure 1.

7.2 Allow both colorimeter and recorder to warm up for 30 minutes. Run a baseline with all reagents, feeding distilled water through the sample line. Adjust dark current and operative opening on colorimeter to obtain suitable baseline.

7.3 Place wash water tubes in sampler in sets of two, leaving every third position vacant. Set sampling time at 1.5 minutes.

7.4 Place NTA standards in sampler in order of increasing or decreasing concentration. Complete filling of sample tray with unknown samples.

7.5 Switch sample line from distilled water to sampler and begin analysis.

8. Calculation

8.1 Prepare standard curve by plotting peak heights of processed NTA standards against known concentrations. Compute concentration of samples by comparing sample peak heights with standard curve.

9. Precision and Accuracy

9.1 In a single laboratory (MDQARL), using surface water samples at concentrations of 0.1, 0.18, 0.27, and 0.44 mg/l, the standard deviations were ±0.01, ±0.004,

±0.004, and ±0.005, respectively. At concentrations of 1.3, 4.0, 5.8, and 7.4 mg/l, the standard deviations were ±0.05, ±0.05, ±0.07, and ±0.1, respectively.

9.2 In a single laboratory (MDQARL), using surface water samples at concentrations of 0.18 and 0.27 mg/l, recoveries were 101% and 106%, respectively. At concentrations of 4.0 and 5.8 mg/l, the recoveries were 98% and 96%, respectively.

Bibliography

1. Thompson, J. E., and Duthie, J. R., "The Biodegradability and Treatment of NTA." Jour. WPCF, *40*, No. 2, 306 (1968).
2. Shumate, K. S. et al, "NTA Removal by Activated Sludge – Field Study." ibid, *42*, No. 4, 631 (1970).
3. Kopp, J. F. and Kroner, R. C., "Trace Metals in Waters of the United States." USDI, FWPCA, DPS, 1014 Broadway, Cincinnati, Ohio 45202.

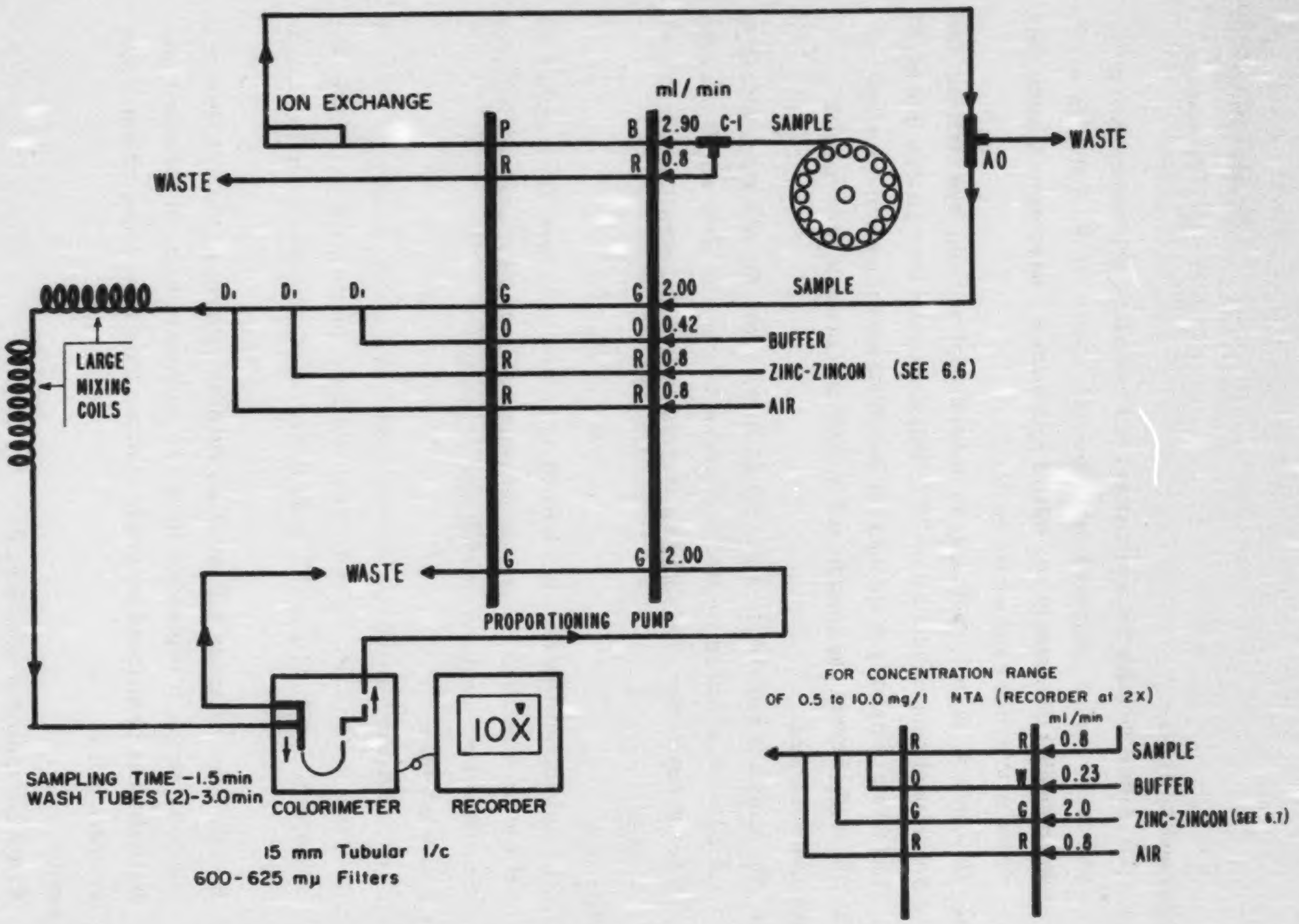
ION EXCHANGE
WASTE
ml/min
P
R
B
R
2.90
0.8
C-I
SAMPLE
A0
WASTE
SAMPLE
D₁
D₁
D₁
G
O
R
R
G
O
R
R
2.00
0.42
0.8
0.8
BUFFER
ZINC-ZINCON (SEE 6.6)
AIR
LARGE MIXING COILS
G
G
2.00
WASTE
PROPORTIONING PUMP
10X
SAMPLING TIME -1.5 min
WASH TUBES (2)-3.0 min
COLORIMETER
RECORDER
15 mm Tubular f/c
600-625 mμ Filters
FOR CONCENTRATION RANGE
OF 0.5 to 10.0 mg/l NTA (RECORDER at 2X)
ml/min
R
O
G
R
R
W
G
R
0.8
0.23
2.0
0.8
SAMPLE
BUFFER
ZINC-ZINCON (SEE 6.7)
AIR

FIGURE 1. NTA MANIFOLD (0.04-1.0 mg/l NTA) AA-I

OIL AND GREASE, Total, Recoverable
(Soxhlet Extraction)

STORET NO. 00550

1. Scope and Application
   1.1 This method includes the measurement of Freon extractable matter from surface and saline waters, industrial and domestic wastes. It is applicable to the determination of relatively non-volatile hydrocarbons, vegetable oils, animal fats, waxes, soaps, greases and related matters.

   1.2 The method is not applicable to measurement of light hydrocarbons that volatilize at temperatures below 70°C. Petroleum fuels from gasoline through #2 fuel oil are completely or substantially lost in the solvent removal operation.

   1.3 The method covers the range from 5 to 1000 mg/l of extractable material.

2. Summary of Method
   2.1 The sample is acidified to a low pH (<2) to remove the oils and greases from solution. After they are isolated by filtration, they are extracted with Freon using a Soxhlet extraction. The solvent is evaporated from the extract and the residue weighed.

3. Definitions
   3.1 The definition of grease and oil is based on the procedure used. The source of the oil and/or grease, and the presence of extractable non-oily matter will influence the material measured and interpretation of results.

4. Sampling and Storage
   4.1 A representative 1 liter sample should be collected in a wide-mouth glass bottle. If analysis is to be delayed for more than a few hours, the sample is preserved by the addition of 5 ml H_2SO_4 or HCl (6.1) at the time of collection and refrigerated at 4°C.

   4.2 Because losses of grease will occur on sampling equipment, the collection of a composite sample is impractical. Individual portions collected at prescribed time intervals must be analyzed separately to obtain the average concentration over an extended period.

5. Apparatus
   5.1 Extraction apparatus consisting of:
      5.1.1 Soxhlet extractor, medium size (Corning No. 3740 or equivalent).
      5.1.2 Soxhlet thimbles, to fit in Soxhlet extractor, (5.1.1).

5.1.3 Flask, 125 ml (Corning No. 4100 or equivalent).

5.1.4 Condenser, Allihn (bulb) type, to fit extractor.

5.1.5 Electric heating mantle.

5.2 Vacuum pump, or other source of vacuum.

5.3 Buchner funnel, 12 cm.

5.4 Filter paper, Whatman No. 40, 11 cm.

5.5 Muslin cloth discs, 11 cm (muslin cloth available at sewing centers). The muslin discs are cut to the size of the filter paper and pre-extracted with Freon before use.

6. Reagents

6.1 Sulfuric acid, 1:1. Mix equal volumes of conc. H_2SO_4 and distilled water. (Conc. hydrochloric acid may be substituted directly for conc. sulfuric for this reagent.)

6.2 Freon TF (or Genesolv D, etc.), registered trademarks for 1,1,2-trichloro-1,2,2,-trifluoroethane, b. p. 48°C.

6.3 Diatomaceous - silica filter aid suspension, 10 g/l in distilled water.

NOTE: Hyflo Super-Cel (Johns-Manville Corp.) or equivalent is used in the preparation of the filter aid suspension.

7. Procedure

7.1 In the following procedure, all steps must be rigidly adhered to if consistent results are to be obtained.

7.2 Mark the sample bottle at the water meniscus for later determination of sample volume. If the sample was not acidified at the time of collection, add 5 ml sulfuric acid or hydrochloric acid (6.1) to the sample bottle. After mixing the sample, check the pH by touching pH-sensitive paper to the cap to insure that the pH is 2 or lower. Add more acid if necessary.

7.3 Prepare a filter consisting of a muslin cloth disc overlaid with filter paper. Place the assembled filter in the Buchner funnel and wet the filter, pressing down the edges to secure a seal. With vacuum on, put 100 ml of the filter aid suspension through the filter and then wash with three 100 ml volumes of distilled water. Continue the vacuum until no more water passes through the filter.

7.4 Filter the acidified sample through the prepared filter pad under vacuum and continue the vacuum until no more water passes through the filter.

7.5 Using forceps, transfer the filter paper and all solid material on the muslin to a watch glass. Wipe the inside and cap of the sample bottle and the inside of the

Buchner funnel with pieces of filter paper soaked in Freon to remove all oil film. Fold the pieces of filter paper and fit them into an extraction thimble. Wipe the watch glass in a similar manner and add the filter paper and all solid matter to the thimble.

7.6 Fill the thimble with small glass beads or glass wool, and dry in an oven at 103°C for *exactly* 30 minutes.

7.7 Weigh the distilling flask (pre-dried in oven at 103°C and stored in desiccator), add the Freon, and connect to the Soxhlet apparatus in which the extraction thimble has been placed. Extract at the rate of 20 cycles per hour for four hours. The four hours is timed from the first cycle.

7.8 Evaporate the solvent from the extraction flask in a water bath at 70°C. Dry by placing the flask on a covered 80°C water bath for 15 minutes. Draw air through the flask by means of an applied vacuum for 1 minute.

7.9 Cool the flask in desiccator for 30 minutes and weigh.

8. Calculation

8.1 $$\text{mg/l total grease} = \frac{R-B}{V}$$

where:

R = residue, gross weight of extraction flask minus the tare weight, in milligrams.

B = blank determination, residue of equivalent volume of extraction solvent, in milligrams.

V = volume of sample, determined by refilling sample bottle to calibration line and correcting for acid addition if necessary, in liters.

9. Precision and Accuracy

9.1 The three oil and grease methods in this manual were tested by a single laboratory (MDQARL) on a sewage. This method determined the oil and grease level in the sewage to be 14.8 mg/l. When 1 liter portions of the sewage were dosed with 14.0 mg of a mixture of #2 fuel oil and Wesson oil, the recovery was 88% with a standard deviation of 1.1 mg.

Bibliography

1. Standard Methods for the Examination of Water and Wastewater, 13th Edition, p 409, Method 209A (1971).
2. Hatfield, W. D., and Symons, G. E., "The Determination of Grease in Sewage", Sewage Works J., *17*, 16 (1945).
3. Blum, K. A., and Taras, M. J., "Determination of Emulsifying Oil in Industrial Wastewater", JWPCF Research Suppl. *40*, R404 (1968).

OIL AND GREASE, Total, Recoverable

(Separatory Funnel Extraction)

STORET NO. 00556

1. Scope and Application

   1.1 This method includes the measurement of Freon extractable matter from surface and saline waters, industrial and domestic wastes. It is applicable to the determination of relatively non-volatile hydrocarbons, vegetable oils, animal fats, waxes, soaps, greases and related matter.

   1.2 The method is not applicable to measurement of light hydrocarbons that volatilize at temperatures below 70°C. Petroleum fuels from gasoline through #2 fuel oils are completely or substantially lost in the solvent removal operation.

   1.3 Some crude oils and heavy fuel oils contain a significant percentage of residue-type materials that are not soluble in Freon. Accordingly, recoveries of these materials will be low.

   1.4 The method covers the range from 5 to 1000 mg/l of extractable material.

2. Summary of Method

   2.1 The sample is acidified to a low pH (<2) and serially extracted with Freon in a separatory funnel. The solvent is evaporated from the extract and the residue weighed.

3. Definitions

   3.1 The definition of grease and oil is based on the procedure used. The source of the oil and/or grease, and the presence of extractable non-oily matter will influence the material measured and interpretation of results.

4. Sampling and Storage

   4.1 A representative sample of 1 liter volume should be collected in a glass bottle. If analysis is to be delayed for more than a few hours, the sample is preserved by the addition of 5 ml H_2SO_4 or HC1 (6.1) at the time of collection and refrigerated at 4°C.

   4.2 Because losses of grease will occur on sampling equipment, the collection of a composite sample is impractical. Individual portions collected at prescribed time intervals must be analyzed separately to obtain the average concentration over an extended period.

5. Apparatus

   5.1 Separatory funnel, 2000 ml, with Teflon stopcock.

   5.2 Vacuum pump, or other source of vacuum.

5.3 Flask, distilling, 125 ml (Corning No. 4100 or equivalent).

5.4 Filter paper, Whatman No. 40, 11 cm.

6. Reagents

6.1 Sulfuric acid, 1:1. Mix equal volumes of conc. H_2SO_4 and distilled water. (Conc. hydrochloric acid may be substituted directly for conc. sulfuric for this reagent).

6.2 Freon TF (or Genesolv D, etc.), registered trademarks for 1,1,2-trichloro-1,2,2,-trifluoroethane, b. p. 48°C.

6.3 Sodium sulfate, anhydrous crystal.

7. Procedure

7.1 Mark the sample bottle at the water meniscus for later determination of sample volume. If the sample was not acidified at time of collection, add 5 ml sulfuric acid or hydrochloric acid (6.1) to the sample bottle. After mixing the sample, check the pH by touching pH-sensitive paper to the cap to insure that the pH is 2 or lower. Add more acid if necessary.

7.2 Pour the sample into a separatory funnel.

7.3 Add 30 ml Freon (6.2) to the sample bottle and rotate the bottle to rinse the sides. Transfer the solvent into the separatory funnel. Extract by shaking vigorously for 2 minutes. Allow the layers to separate.

7.4 Tare a distilling flask (pre-dried in an oven at 103°C and stored in a desiccator), and filter the solvent layer into the flask through a funnel containing solvent moistened filter paper.

NOTE: An emulsion that fails to dissipate can be broken by pouring about 1 g sodium sulfate (6.3) into the filter paper cone and draining the emulsion through the salt. Additional 1 g portions can be added to the cone as required.

7.5 Repeat (7.3 and 7.4) twice more, with additional portions of fresh solvent, combining all solvent in the distilling flask.

7.6 Rinse the tip of the separatory funnel, the filter paper, and then the funnel with a total of 10-20 ml Freon and collect the rinsings in the flask.

7.7 Evaporate the solvent from the extraction flask in a water bath at 70°C. Dry by placing the flask on a covered 80°C water bath for 15 minutes. Draw air through the flask by means of an applied vacuum for 1 minute.

7.8 Cool in desiccator for 30 minutes and weigh.

8. Calculation

8.1 mg/l total oil and grease $= \frac{R-B}{V}$

where:

R = residue, gross weight of extraction flask minus the tare weight, in milligrams.

B = blank determination, residue of equivalent volume of extraction solvent, in milligrams.

V = volume of sample, determined by refilling sample bottle to calibration line and correcting for acid addition if necessary, in liters.

9. Precision and Accuracy

9.1 The three oil and grease methods in this manual were tested by a single laboratory (MDQARL) on a sewage. This method determined the oil and grease level in the sewage to be 12.6 mg/l. When 1 liter portions of the sewage were dosed with 14.0 mg of a mixture of #2 fuel oil and Wesson oil, the recovery was 93% with a standard deviation of 0.9 mg.

Bibliography

1. Standard Methods for the Examination of Water and Wastewater, 13th Edition, p 254, Method 137 (1971).
2. Blum, K. A., and Taras, M. J., "Determination of Emulsifying Oil in Industrial Wastewater", JWPCF Research Suppl. *40*, R404 (1968).

OIL AND GREASE, Total, Recoverable
(Infrared)

STORET NO. 00560

Scope and Application

1.1 This method includes the measurement of Freon extractable matter from surface and saline waters, industrial and domestic wastes. It is applicable to the determination of hydrocarbons, vegetable oils, animal fats, waxes, soaps, greases and related matter.

1.2 The method is applicable to measurement of most light petroleum fuels, although loss of about half of any gasoline present during the extraction manipulations can be expected.

1.3 The method covers the range from 0.2 to 1000 mg/l of extractable material.

2. Summary of Method

2.1 The sample is acidified to a low pH (<2) and extracted with Freon. The oil and grease is determined by comparison of the infrared absorbance of the sample extract with standards.

3. Definitions

3.1 The definition of grease and oil is based on the procedure used. The source of the oil and/or grease, and the presence of extractable non-oily matter will influence the material measured and interpretation of results.

3.2 An "Unknown Oil" is defined as one for which a representative sample of the oil or grease is not available for preparation of a standard. Examples of unknown oils are the oil and grease in a mixed sewage or an unidentified oil slick on a surface water.

3.3 A "Known Oil" is defined as a sample of oil and/or grease that represents the only material of that type used or manufactured in the processes represented by a wastewater.

4. Sampling and Storage

4.1 A representative sample of 1 liter volume should be collected in a glass bottle. If analysis is to be delayed for more than a few hours, the sample is preserved by the addition of 5 ml H_2SO_4 or HC1 (6.1) at the time of collection and refrigerated at 4°C.

4.2 Because losses of grease will occur on sampling equipment, the collection of a composite sample is impractical. Individual portions collected at prescribed time intervals must be analyzed separately to obtain the average concentration over an extended period.

5. Apparatus

5.1 Separatory funnel, 2000 ml, with Teflon stopcock.

5.2 Infrared spectrophotometer, double beam, recording.

5.3 Cells, quartz, 10 mm, 50 mm, and 100 mm path length.

5.4 Syringes, 10, 25, 50, 100 microliter capacity.

5.5 Filter paper, Whatman No. 40, 11 cm.

6. Reagents

6.1 Sulfuric acid, 1:1. Mix equal volumes of conc. H_2SO_4 and distilled water. (Conc. hydrochloric acid may be substituted directly for conc. sulfuric for this reagent.)

6.2 Freon TF (or Genesolv D, etc.), registered trademarks for 1,1,2-trichloro-1,2,2,-trifluoroethane, b. p. 48°C.

6.3 Sodium sulfate, anhydrous crystal.

6.4 Known oil reference standard: Accurately weigh about 0.05 g of known oil directly into a 100 ml volumetric flask. Add 80 ml Freon and dissolve the oil. If, as in the case of a heavy fuel oil, all the oil does not go into solution, let stand overnight. The next day filter through paper into another 100 ml volumetric and dilute to mark. Treat calculations as if all oil had gone into solution.

6.5 Unknown oil reference standard ($10\mu l$ = 7.69 mg oil): Pipette 15.0 ml n-hexadecane, 15.0 ml isooctane, and 10.0 ml benzene into a 50 ml glass stoppered bottle. Assume the specific gravity of this mixture to be 0.769 and maintain the integrity of the mixture by keeping stoppered except when withdrawing aliquots.

7. Procedure

7.1 Mark the sample bottle at the water meniscus for later determination of sample volume. If the sample was not acidified at time of collection, add 5 ml sulfuric or hydrochloric acid (6.1) to the sample bottle. After mixing the sample, check the pH by touching pH-sensitive paper to the cap to insure that the pH is 2 or lower. Add more acid if necessary.

7.2 Pour the sample into a separatory funnel.

7.3 Add 30 ml Freon (6.2) to the sample bottle and rotate the bottle to rinse the sides. Transfer the solvent into the separatory funnel. Extract by shaking vigorously for 2 minutes. Allow the layers to separate.

7.4 Filter the solvent layer into a 100 ml volumetric flask through a funnel containing solvent-moistened filter paper.

NOTE 1: An emulsion that fails to dissipate can be broken by pouring about 1 g sodium sulfate (6.3) into the filter paper cone and draining the emulsion through the salt. Additional 1 g portions can be added to the cone as required.

7.5 Repeat (7.3 and 7.4) twice more with 30 ml portions of fresh solvent, combining all solvent in the volumetric flask.

7.6 Rinse the tip of the separatory funnel, filter paper, and the funnel with a total of 10-20 ml Freon and collect the rinsings in the flask. Dilute the extract to 100 ml, and stopper the flask.

7.7 Select appropriate calibration standards and cell pathlength according to the following table of approximate working ranges:

Pathlength	Range
1 cm	4-40 mg
5 cm	0.5-8 mg
10 cm	0.1-4 mg

Prepare calibration standards by pipetting appropriate amounts of the known oil reference standard (6.4) into 100 ml volumetric flasks and diluting to mark with Freon. Alternately, transfer appropriate amounts of the unknown oil reference standard (6.5), using microliter syringes, to 100 ml volumetric flasks and diluting to mark with Freon.

NOTE 2: Ten microliters of the unknown oil is equivalent to 7.69 mg per 100 ml Freon, and 7.69 mg per sample volume.

7.8 Scan standards and samples from 3200 cm^{-1} to 2700 cm^{-1} with Freon in the reference beam and record the results on absorbance paper. The absorbances of samples and standards are measured by constructing a straight baseline over the range of the scan and measuring the absorbance of the peak maximum at 2930 cm^{-1} and subtracting the baseline absorbance at that point. If the absorbance exceeds 0.8 for a sample, select a shorter pathlength or dilute as required.

NOTE 3: Caution must be exercised in the selection of the 2930 cm^{-1} peak, as it may not always be the largest peak in the range of the scan. For an example of a typical oil spectrum and baseline construction, see Gruenfeld(3).

7.9 Use a calibration plot of absorbance vs. mg oil prepared from the standards to determine the mg oil in the sample solution.

8. Calculation

8.1 mg/l total oil and grease = $\frac{R \times D}{V}$

where:

R = oil in solution, determined from calibration plot, in milligrams.

D = extract dilution factor, if used.

V = volume of sample, determined by refilling sample bottle to calibration line and correcting for acid addition if necessary, in liters.

9. Precision and Accuracy

9.1 The three oil and grease methods in this manual were tested by a single laboratory (MDQARL) on a sewage. This method determined the oil and grease level in the sewage to be 17.5 mg/l. When 1 liter portions of the sewage were dosed with 14.0 mg of a mixture of #2 fuel oil and Wesson oil, the recovery was 99% with a standard deviation of 1.4 mg.

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ORGANIC CARBON
(Total and Dissolved)

STORET NO. Total 00680
Dissolved 00681

1. Scope and Application

1.1 This method includes the measurement of organic carbon in drinking, surface, and saline waters, domestic and industrial wastes. Exclusions are noted under Definitions and Interferences.

1.2 The method is most applicable to measurement of organic carbon above 1 mg/l.

2. Summary of Method

2.1 Organic carbon in a sample is converted to carbon dioxide (CO_2) by catalytic combustion or wet chemical oxidation. The CO_2 formed can be measured directly by an infrared detector or converted to methane (CH_4) and measured by a flame ionization detector. The amount of CO_2 or CH_4 is directly proportional to the concentration of carbonaceous material in the sample.

3. Definitions

3.1 The carbonaceous analyzer measures all of the carbon in a sample. Because of various properties of carbon-containing compounds in liquid samples, preliminary treatment of the sample prior to analysis dictates the definition of the carbon as it is measured. Forms of carbon that are measured by the method are:

A) soluble, nonvolatile organic carbon; for instance, natural sugars.
B) soluble, volatile organic carbon; for instance, mercaptans.
C) insoluble, partially volatile carbon; for instance, oils.
D) insoluble, particulate carbonaceous materials, for instance, cellulose fibers.
E) soluble or insoluble carbonaceous materials adsorbed or entrapped on insoluble inorganic suspended matter; for instance, oily matter adsorbed on silt particles.

3.2 The final usefulness of the carbon measurement is in assessing the potential oxygen-demanding load of organic material on a receiving stream. This statement applies whether the carbon measurement is made on a sewage plant effluent, industrial waste, or on water taken directly from the stream. In this light, carbonate and bicarbonate carbon are not a part of the oxygen demand in the stream and therefore should be discounted in the final calculation or removed prior to analysis. The manner of preliminary treatment of the sample and instrument settings defines the types of carbon which are measured. Instrument manufacturer's instructions should be followed.

4. Sample Handling and Preservation

4.1 Sampling and storage of samples in glass bottles is preferable. Sampling and storage in plastic bottles such as conventional polyethylene and cubitainers is permissible if it is established that the containers do not contribute contaminating organics to the samples.

NOTE 1: A brief study performed in the EPA Laboratory indicated that distilled water stored in new, one quart cubitainers did not show any increase in organic carbon after two weeks exposure.

4.2 Because of the possibility of oxidation or bacterial decomposition of some components of aqueous samples, the lapse of time between collection of samples and start of analysis should be kept to a minimum. Also, samples should be kept cool (4°C) and protected from sunlight and atmospheric oxygen.

4.3 In instances where analysis cannot be performed within two hours (2 hours) from time of sampling, it is recommended that the sample is acidified ($pH \leq 2$) with HCl or H_2SO_4.

5. Interferences

5.1 Carbonate and bicarbonate carbon represent an interference under the terms of this test and must be removed or accounted for in the final calculation.

5.2 This procedure is applicable only to homogeneous samples which can be injected into the apparatus reproducibly by means of a microliter type syringe or pipette. The openings of the syringe or pipette limit the maximum size of particles which may be included in the sample.

6. Apparatus

6.1 Apparatus for blending or homogenizing samples: Generally, a Waring-type blender is satisfactory.

6.2 Apparatus for total and dissolved organic carbon:

6.2.1 A number of companies manufacture systems for measuring carbonaceous material in liquid samples. Considerations should be made as to the types of samples to be analyzed, the expected concentration range, and forms of carbon to be measured.

6.2.2 No specific analyzer is recommended as superior. However, analyzers which have been found to be reliable are the Dow-Beckman Carbonaceous Analyzer Model No. 915, the Dohrmann Envirotech DC-50 Carbon Analyzer and the Oceanography International Total Carbon Analyzer.

7. Reagents

7.1 Distilled water used in preparation of standards and for dilution of samples should be ultra pure to reduce the size of the blank. Carbon dioxide-free, double distilled water is recommended. Ion exchanged waters are not recommended because of the possibilities of contamination with organic materials from the resins.

7.2 Potassium hydrogen phthalate, stock solution, 1000 mg carbon/liter: Dissolve 0.2128 g of potassium hydrogen phthalate (Primary Standard Grade) in distilled water and dilute to 100.0 ml.

NOTE 2: Sodium oxalate and acetic acid are not recommended as stock solutions.

7.3 Potassium hydrogen phthalate, standard solutions: Prepare standard solutions from the stock solution by dilution with distilled water.

7.4 Carbonate-bicarbonate, stock solution, 1000 mg carbon/liter: Weigh 0.3500 g of sodium bicarbonate and 0.4418 g of sodium carbonate and transfer both to the same 100 ml volumetric flask. Dissolve with distilled water.

7.5 Carbonate-bicarbonate, standard solution: Prepare a series of standards similar to step 7.3.

NOTE 3: This standard is not required by some instruments.

7.6 Blank solution: Use the same distilled water (or similar quality water) used for the preparation of the standard solutions.

8. Procedure

8.1 Follow instrument manufacturer's instructions for calibration, procedure, and calculations.

8.2 For calibration of the instrument, it is recommended that a series of standards encompassing the expected concentration range of the samples be used.

9. Precision and Accuracy

9.1 Twenty-eight analysts in twenty-one laboratories analyzed distilled water solutions containing exact increments of oxidizable organic compounds, with the following results:

Increment as TOC mg/liter	Precision as Standard Deviation TOC, mg/liter	Accuracy as Bias, %	Bias, mg/liter
4.9	3.93	+15.27	+0.75
107	8.32	+ 1.01	+1.08

(FWPCA Method Study 3, Demand Analyses)

pH

STORET NO. 00400

1. Scope and Application

   1.1 This method is applicable to drinking, surface, and saline waters, domestic and industrial wastes.

2. Summary of Method

   2.1 The pH of a sample is an electrometric measurement, using either a glass electrode in combination with a reference potential (saturated calomel electrode) or a combination electrode (glass and reference).

3. Comments

   3.1 The sample must be analyzed as soon as practical; preferably within a few hours. Do not open sample bottle before analyses.

   3.2 Oil and greases, by coating the pH electrode, may interfere by causing sluggish response.

   3.3 At least three buffer solutions must be used to initially standardize the instrument. They should cover the pH range of the samples to be measured.

   3.4 Field pH measurements using comparable instruments are reliable.

4. Precision and Accuracy

   4.1 Forty-four analysts in twenty laboratories analyzed six synthetic water samples containing exact increments of hydrogen-hydroxyl ions, with the following results:

Increment as pH Units	Precision as Standard Deviation pH Units	Accuracy as	
		Bias, %	Bias, pH Units
3.5	0.10	–0.29	–0.01
3.5	0.11	–0.00	
7.1	0.20	+1.01	+0.07
7.2	0.18	–0.03	–0.002
8.0	0.13	–0.12	–0.01
8.0	0.12	+0.16	+0.01

(FWPCA Method Study 1, Mineral and Physical Analyses)

4.2 In a single laboratory (MDQARL), using surface water samples at an average pH of 7.7, the standard deviation was ±0.1.

5. Reference

5.1 The procedure to be used for this determination is found in:

Standard Methods for the Examination of Water and Wastewater, 13th Edition, p 276, Method 144 A (1971).

ASTM Standards, Part 23, Water: Atmospheric Analysis, p 186, Method D1293-65 (1973).

PHENOLICS

(4-AAP Method With Distillation)

STORET NO. 32730

1. Scope and Application

   1.1 This method is applicable to the analysis of drinking, surface, and saline waters, domestic and industrial wastes.

   1.2 The method is capable of measuring phenolic materials from about 5 μg/l to about 1000 μg/l when the colored end product is extracted and concentrated in a solvent phase using phenol as a standard.

   1.3 The method is capable of measuring phenolic materials that contain more than 50 μg/l in the aqueous phase (without solvent extraction) using phenol as a standard.

   1.4 It is not possible to use this method to differentiate between different kinds of phenols.

2. Summary of Method

   2.1 Phenolic materials react with 4-aminoantipyrine in the presence of potassium ferricyanide at a pH of 10 to form a stable reddish-brown colored antipyrine dye. The amount of color produced is a function of the concentration of phenolic material.

3. Comments

   3.1 For most samples a preliminary distillation is required to remove interfering materials.

   3.2 Color response of phenolic materials with 4-amino-antipyrine is not the same for all compounds. Because phenolic type wastes usually contain a variety of phenols, it is not possible to duplicate a mixture of phenols to be used as a standard. For this reason phenol itself has been selected as a standard and any color produced by the reaction of other phenolic compounds is reported as phenol. This value will represent the minimum concentration of phenolic compounds present in the sample.

   3.3 Control of the pH of the reaction may be accomplished using the procedure detailed in Standard Methods (p 506, 13th Edition), or ASTM, Part 23, p 535 (Nov. 1973), or by use of the ammonium hydroxide-ammonium chloride buffer used in the water hardness test Standard Methods, 13th Edition, p 181, (1971).

4. Precision and Accuracy

   4.1 Using the extraction procedure for concentration of color, six laboratories analyzed samples at concentrations of 9.6, 48.3, and 93.5 μg/l. Standard deviations were, respectively, ±0.99, ±3.1 and ±4.2 μg/l.

4.2 Using the direct photometric procedure, six laboratories analyzed samples at concentrations of 4.7, 48.2 and 97.0 mg/l. Standard deviations were ±0.18, ±0.48 and ±1.58 mg/l, respectively.

5. References

5.1 The procedure to be used for this determination is found in:

Standard Methods for the Examination of Water and Wastewater, 13th Edition, p 501-510, Method No. 222 through 222E (1971).

ASTM Standards, Part 23, Water; Atmospheric Analysis, p 535, Method D-1783-70 (1973).

PHENOLICS

(Automated 4-AAP Method With Distillation)

STORET NO. 32730

1. Scope and Application
   - 1.1 This method is applicable to the analysis of drinking, surface, and saline waters, domestic and industrial wastes.
   - 1.2 The method is capable of measuring phenolic materials from 2 to 500 μg/l in the aqueous phase using phenol as a standard. The working ranges are 2 to 200 μg/l and 10 to 500 μg/l.
2. Summary of Method
   - 2.1 This automated method is based on the distillation of phenol and subsequent reaction of the distillate with alkaline ferricyanide and 4-aminoantipyrine to form a red complex which is measured at 505 or 520 nm. The same manifold is used with the AAI or AAII.
3. Sample Handling and Preservation
   - 3.1 Biological degradation is inhibited by the addition of 1 g/l of copper sulfate to the sample and acidification to a pH of less than 4 with phosphoric acid. The sample should be kept at 5-10°C and analyzed within 24 hours after collection.
4. Interference
   - 4.1 Interferences from sulfur compounds are eliminated by acidifying the sample to a pH of less than 4.0 with H_3PO_4 and aerating briefly by stirring and adding $CuSO_4$.
   - 4.2 Oxidizing agents such as chlorine, detected by the liberation of iodine upon acidification in the presence of potassium iodide, are removed immediately after sampling by the addition of an excess of ferrous ammonium sulfate (6.5). If chlorine is not removed, the phenolic compounds may be partially oxidized and the results may be low.
   - 4.3 Background contamination from plastic tubing and sample containers is eliminated by filling the wash receptacle by siphon (using Kel-F tubing) and using glass tubes for the samples and standards.
5. Apparatus
   - 5.1 Technicon AutoAnalyzer (I or II)
     - 5.1.1 Sampler.
     - 5.1.2 Manifold.

5.1.3 Proportioning pump II or III.

5.1.4 Heating bath with distillation coil.

5.1.5 Distillation head.

5.1.6 Colorimeter equipped with a 50 mm flow cell and 505 or 520 nm filter.

5.1.7 Recorder.

6. Reagents

6.1 Distillation reagent: Add 100 ml of conc. phosphoric acid (85% H_3PO_4) to 800 ml of distilled water, cool and dilute to 1 liter.

6.2 Buffered potassium ferricyanide: Dissolve 2.0 g potassium ferricyanide, 3.1 g boric acid and 3.75 g potassium chloride in 800 ml of distilled water. Adjust to pH of 10.3 with 1 N sodium hydroxide (6.3) and dilute to 1 liter. Add 0.5 ml of Brij-35. Prepare fresh weekly.

6.3 Sodium hydroxide (1N): Dissolve 40 g NaOH in 500 ml of distilled water, cool and dilute to 1 liter.

6.4 4-Aminoantipyrine: Dissolve 0.65 g of 4-aminoantipyrine in 800 ml of distilled water and dilute to 1 liter. Prepare fresh each day.

6.5 Ferrous ammonium sulfate: Dissolve 1.1 g ferrous ammonium sulfate in 500 ml distilled water containing 1 ml H_2SO_4 and dilute to 1 liter with freshly boiled and cooled distilled water.

6.6 Stock phenol: Dissolve 1.00 g phenol in 500 ml of distilled water and dilute to 1000 ml. Add 1 g $CuSO_4$ and 0.5 ml conc. H_3PO_4 as preservative. 1.0 ml = 1.0 mg phenol.

6.7 Standard phenol solution A: Dilute 10.0 ml of stock phenol solution (6.6) to 1000 ml. 1.0 ml = 0.01 mg phenol.

6.8 Standard phenol solution B: Dilute 100.0 ml of standard phenol solution A (6.7) to 1000 ml with distilled water. 1.0 ml = 0.001 mg phenol.

6.9 Standard solution C: Dilute 100.0 ml of standard phenol solution B (6.8) to 1000 ml with distilled water. 1.0 ml = 0.0001 mg phenol.

6.10 Using standard solution A, B or C prepare the following standards in 100 ml volumetric flasks. Each standard should be preserved by adding 0.1 g $CuSO_4$ and 2 drops of conc. H_3PO_4 to 100.0 ml.

ml of Standard Solution	Conc. μg/l
Solution C	
1.0	1.0
2.0	2.0
3.0	3.0
5.0	5.0
Solution B	
1.0	10.0
2.0	20.0
5.0	50.0
10.0	100.0
Solution A	
2	200
3	300
5	500

7. Procedure

7.1 Set up the manifold as shown in Figures 1 or 2.

7.2 Fill the wash receptacle by siphon. Use Kel-F tubing with a fast flow (1 liter/hr).

7.3 Allow colorimeter and recorder to warm up for 30 minutes. Run a baseline with all reagents, feeding distilled water through the sample line. Use polyethylene tubing for sample line. When new tubing is used, about 2 hours may be required to obtain a stable baseline. This two hour time period may be necessary to remove the residual phenol from the tubing.

7.4 Place appropriate phenol standards in sampler in order of decreasing concentration. Complete loading of sampler tray with unknown samples, using glass tubes. NOTE 1: If samples have not been preserved as instructed in (3.1), add 0.1 g $CuSO_4$ and 2 drops of conc. H_3PO_4 to 100 ml of sample.

7.5 Switch sample line from distilled water to sampler and begin analysis.

8. Calculation

8.1 Prepare standard curve by plotting peak heights of standards against concentration values. Compute concentration of samples by comparing sample peak heights with standards.

9. Precision and Accuracy

9.1 In a single laboratory (MDQARL), using sewage samples at concentrations of 3.8, 15, 43 and 89 μg/l, the standard deviations were ±0.5, ±0.6, ±0.6 and ±1.0 μg/l, respectively. At concentrations of 73, 146, 299 and 447 μg/l, the standard deviations were ±1.0, ±1.8, ±4.2 and ±5.3 μg/l, respectively.

9.2 In a single laboratory (MDQARL), using sewage samples at concentrations of 5.3 and 82 μg/l, the recoveries were 78% and 98%. At concentrations of 168 and 489 μg/l, the recoveries were 97% and 98%, respectively.

Bibliography

1. Technicon AutoAnalyzer II Methodology, Industrial Method No. 127-71W, AAII.
2. Standard Methods for the Examination of Water and Wastewater, 13th Edition, p 501, American Public Health Association, Inc., New York (1971).

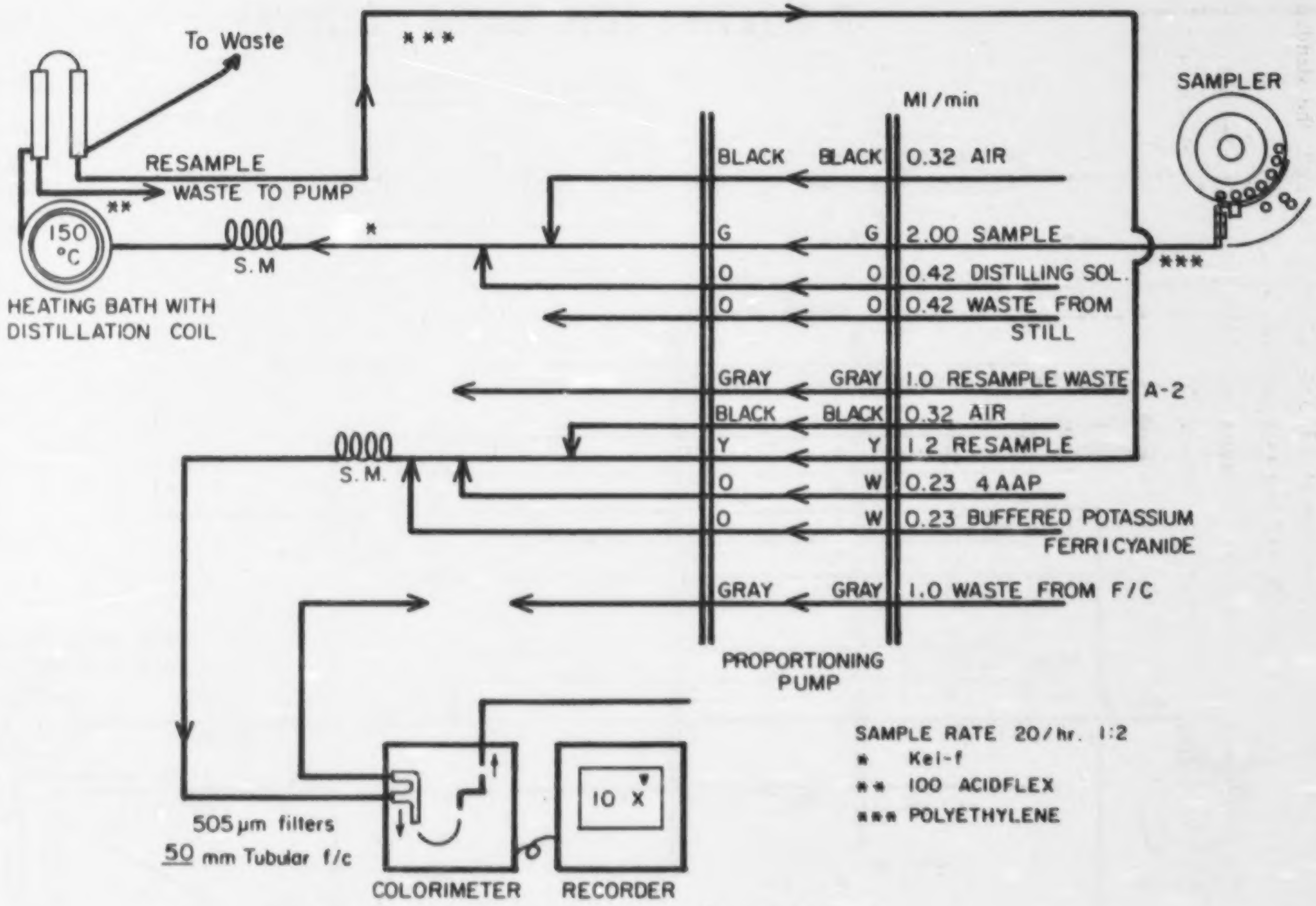
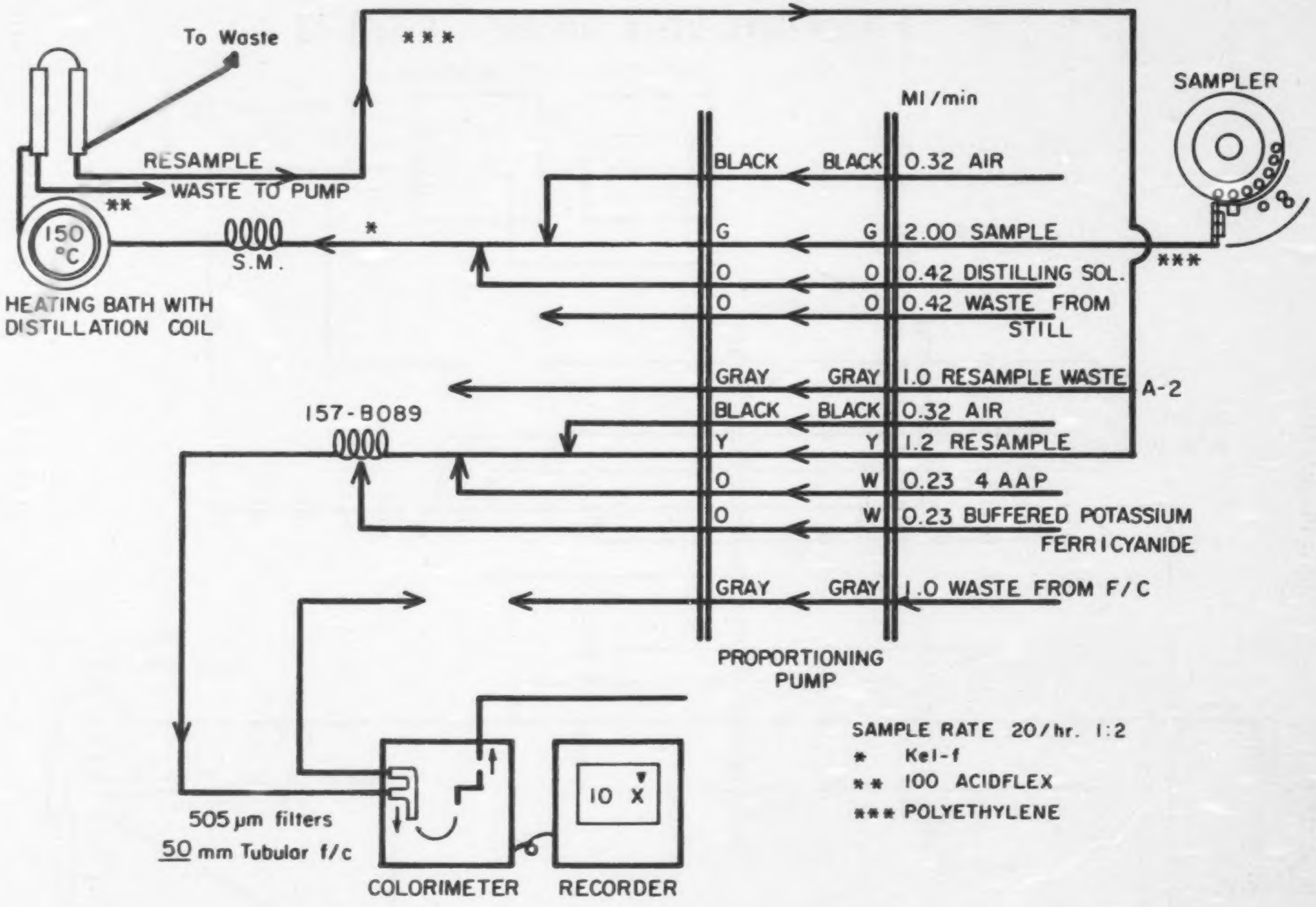

To Waste
* * *
SAMPLER
Ml / min
RESAMPLE
WASTE TO PUMP
**
150 °C
S.M
*
HEATING BATH WITH
DISTILLATION COIL
BLACK
BLACK
0.32 AIR
G
G
2.00 SAMPLE
***
O
O
0.42 DISTILLING SOL.
O
O
0.42 WASTE FROM
STILL
GRAY
GRAY
1.0 RESAMPLE WASTE
A-2
BLACK
BLACK
0.32 AIR
Y
Y
1.2 RESAMPLE
S.M.
O
W
0.23 4 AAP
O
W
0.23 BUFFERED POTASSIUM
FERRICYANIDE
GRAY
GRAY
1.0 WASTE FROM F/C
PROPORTIONING
PUMP
SAMPLE RATE 20/hr. 1:2
* Kel-f
** 100 ACIDFLEX
*** POLYETHYLENE
10 X
505 μm filters
50 mm Tubular f/c
COLORIMETER
RECORDER

FIGURE 1. PHENOL AUTO ANALYZER I



To Waste
* * *
RESAMPLE
WASTE TO PUMP
**
150 °C
S.M.
*
HEATING BATH WITH DISTILLATION COIL
SAMPLER
Ml /min
***
BLACK
BLACK
0.32 AIR
G
G
2.00 SAMPLE
O
O
0.42 DISTILLING SOL.
O
O
0.42 WASTE FROM STILL
GRAY
GRAY
1.0 RESAMPLE WASTE
A-2
BLACK
BLACK
0.32 AIR
Y
Y
1.2 RESAMPLE
O
W
0.23 4 AAP
O
W
0.23 BUFFERED POTASSIUM FERRICYANIDE
GRAY
GRAY
1.0 WASTE FROM F/C
157-B089
PROPORTIONING PUMP
505 μm filters
50 mm Tubular f/c
10 X
COLORIMETER
RECORDER
SAMPLE RATE 20/hr. 1:2
* Kel-f
** 100 ACIDFLEX
*** POLYETHYLENE

FIGURE 2. PHENOL AUTO ANALYZER II

PHOSPHORUS, ALL FORMS

(Single Reagent Method)

STORET NO. See Section 4

1. Scope and Application

   1.1 These methods cover the determination of specified forms of phosphorus in drinking, surface, and saline waters, domestic and industrial wastes. They may be applicable to sediment-type samples, sludges, algal blooms, etc., but sufficient data is not available at this time to warrant such usage when measurements for phosphorus content are required.

   1.2 The methods are based on reactions that are specific for the orthophosphate ion. Thus, depending on the prescribed pre-treatment of the sample, the various forms of phosphorus given in Figure 1 may be determined. These forms are, in turn, defined in Section 4.

      1.2.1 Except for in-depth and detailed studies, the most commonly measured forms are phosphorus and dissolved phosphorus, and orthophosphate and dissolved orthophosphate. Hydrolyzable phosphorus is normally found only in sewage-type samples and insoluble forms of phosphorus, as noted, are determined by calculation.

   1.3 The methods are usable in the 0.01 to 0.5 mg P/l range.

2. Summary of Method

   2.1 Ammonium molybdate and antimony potassium tartrate react in an acid medium with dilute solutions of phosphorus to form an antimony-phospho-molybdate complex. This complex is reduced to an intensely blue-colored complex by ascorbic acid. The color is proportional to the phosphorus concentration.

   2.2 Only orthophosphate forms a blue color in this test. Polyphosphates (and some organic phosphorus compounds) may be converted to the orthophosphate form by sulfuric-acid-hydrolysis. Organic phosphorus compounds may be converted to the orthophosphate form by persulfate digestion(2).

3. Sample Handling and Preservation

   3.1 If benthic deposits are present in the area being sampled, great care should be taken not to include these deposits.

   3.2 Sample containers may be of plastic material, such as cubitainers, or of Pyrex glass.

   3.3 If the analysis cannot be performed the same day of collection, the sample should

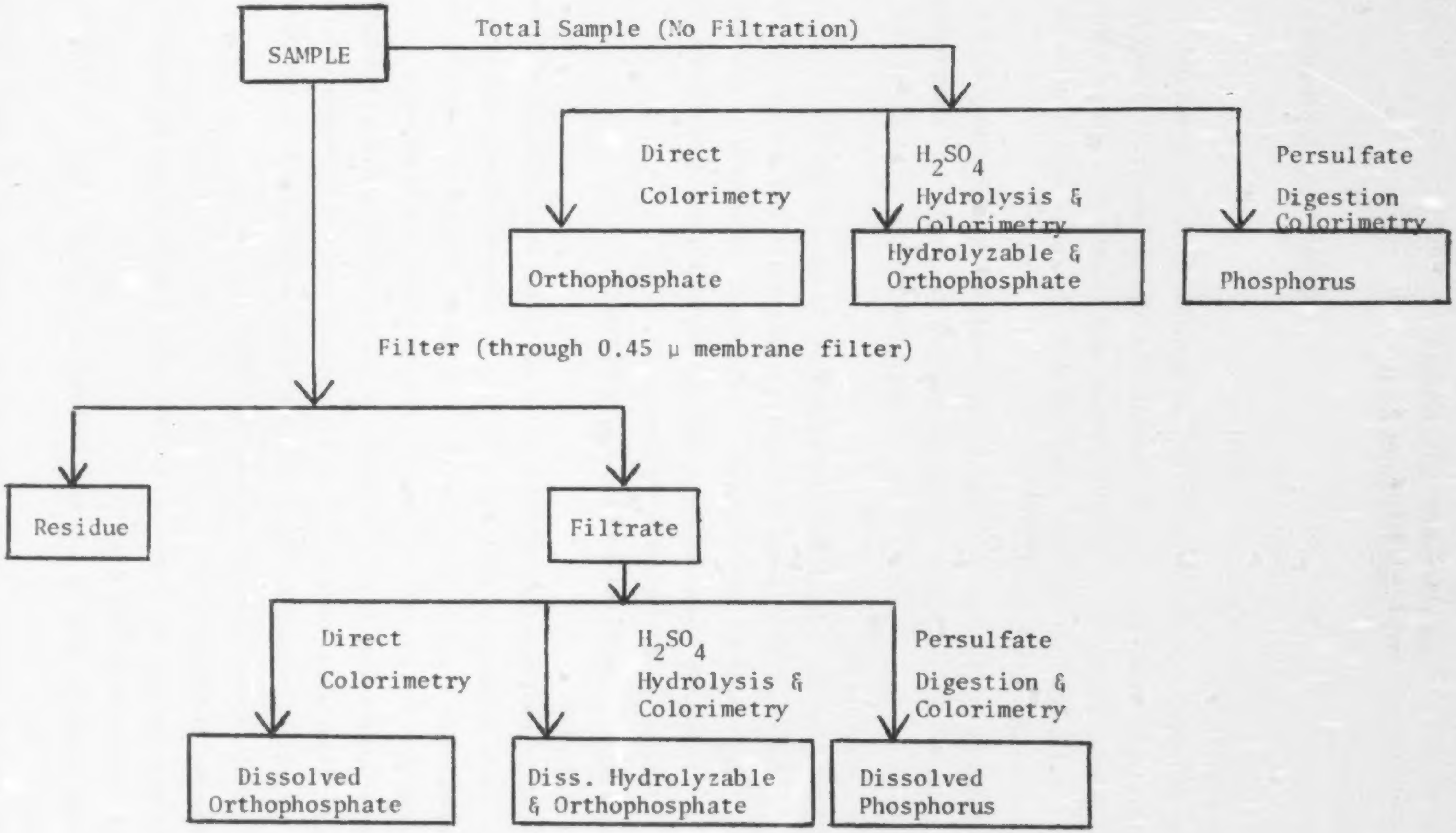

SAMPLE
Total Sample (No Filtration)
Direct
Colorimetry
Orthophosphate
H_2SO_4
Hydrolysis &
Colorimetry
Hydrolyzable &
Orthophosphate
Persulfate
Digestion
Colorimetry
Phosphorus
Filter (through 0.45 μ membrane filter)
Residue
Filtrate
Direct
Colorimetry
Dissolved
Orthophosphate
H_2SO_4
Hydrolysis &
Colorimetry
Diss. Hydrolyzable
& Orthophosphate
Persulfate
Digestion &
Colorimetry
Dissolved
Phosphorus

FIGURE 1. ANALYTICAL SCHEME FOR DIFFERENTIATION OF PHOSPHORUS FORMS

be preserved by the addition of 2 ml conc. H_2SO_4 or 40 mg $HgCl_2$ per liter and refrigeration at 4°C. Note $HgCl_2$ interference under (5.4).

4. Definitions and Storet Numbers

4.1 Total Phosphorus (P) – all of the phosphorus present in the sample, regardless of form, as measured by the persulfate digestion procedure. (00665)

4.1.1 Total Orthophosphate (P, ortho) – inorganic phosphorus $[(PO_4)^{-3}]$ in the sample as measured by the direct colorimetric analysis procedure. (70507)

4.1.2 Total Hydrolyzable Phosphorus (P, hydro) – phosphorus in the sample as measured by the sulfuric acid hydrolysis procedure, and minus pre-determined orthophosphates. This hydrolyzable phosphorus includes polyphosphorus. $[(P_2O_7)^{-4}$, $(P_3O_{10})^{-5}$, etc.] + some organic phosphorus. (00669)

4.1.3 Total Organic Phosphorus (P, org) – phosphorus (inorganic + oxidizable organic) in the sample measured by the persulfate digestion procedure, and minus hydrolyzable phosphorus and orthophosphate. (00670)

4.2 Dissolved Phosphorus (P–D) – all of the phosphorus present in the filtrate of a sample filtered through a phosphorus-free filter of 0.45 micron pore size and measured by the persulfate digestion procedure. (00666)

4.2.1 Dissolved Orthophosphate (P–D, ortho) – as measured by the direct colorimetric analysis procedure. (00671)

4.2.2 Dissolved Hydrolyzable Phosphorus (P–D, hydro) – as measured by the sulfuric acid hydrolysis procedure and minus pre-determined dissolved orthophosphates. (00672)

4.2.3 Dissolved Organic Phosphorus (P–D, org) – as measured by the persulfate digestion procedure, and minus dissolved hydrolyzable phosphorus and orthophosphate. (00673)

4.3 The following forms, when sufficient amounts of phosphorus are present in the sample to warrant such consideration, may be calculated:

4.3.1 Insoluble Phosphorus (P-I) = (P) - (P-D). (00667)

4.3.1.1 Insoluble orthophosphate (P–I, ortho) = (P, ortho) – (P–D, ortho). (00674)

4.3.1.2 Insoluble Hydrolyzable Phosphorus (P–I, hydro) = (P, hydro) – (P–D, hydro). (00675)

4.3.1.3 Insoluble Organic Phosphorus (P–I, org) = (P, org) – (P–D, org). (00676)

4.4 All phosphorus forms shall be reported as P, mg/l, to the third place.

5. Interferences

5.1 It is reported that no interference is caused by copper, iron, or silicate at concentrations many times greater than their reported concentration in sea water. However, high iron concentrations can cause precipitation of and subsequent loss of phosphorus.

5.2 The salt error for samples ranging from 5 to 20% salt content was found to be less than 1%.

5.3 Arsenate is determined similarily to phosphorus and should be considered when present in concentrations higher than phosphorus. However, at concentrations found in sea water, it does not interfere.

5.4 Mercury chloride, used as a preservative, interferes when the chloride level of the sample is low (<50 mg Cl/l). This interference is overcome by spiking samples with a minimum of 50 mg/l of sodium chloride.

6. Apparatus

6.1 Photometer – A spectrophotometer or filter photometer suitable for measurements at 650 or 880 nm with a light path of 1 cm or longer.

6.2 Acid-washed glassware: All glassware used should be washed with hot 1:1 HCl and rinsed with distilled water. The acid-washed glassware should be filled with distilled water and treated with all the reagents to remove the last traces of phosphorus that might be adsorbed on the glassware. Preferably, this glassware should be used only for the determination of phosphorus and after use it should be rinsed with distilled water and kept covered until needed again. If this is done, the treatment with 1:1 HCl and reagents is only required occasionally. *Commercial detergents should never be used.*

7. Reagents

7.1 Sulfuric acid solution, 5N: Dilute 70 ml of conc. H_2SO_4 with distilled water to 500 ml.

7.2 Antimony potassium tartrate solution: Weigh 1.3715 g $K(SbO)C_4H_4O_6 \cdot 1/2 H_2O$, dissolve in 400 ml distilled water in 500 ml volumetric flask, dilute to volume. Store at 4°C in a dark, glass-stoppered bottle.

7.3 Ammonium molybdate solution: Dissolve 20 g $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ in 500 ml of distilled water. Store in a plastic bottle at 4°C.

7.4 Ascorbic acid, 0.1 M: Dissolve 1.76 g of ascorbic acid in 100 ml of distilled water. The solution is stable for about a week if stored at 4°C.

7.5 Combined reagent: Mix the above reagents in the following proportions for 100 ml of the mixed reagent: 50 ml of 5N H_2SO_4, (7.1), 5 ml of antimony potassium tartrate solution, (7.2), 15 ml of ammonium molybdate solution, (7.3), and 30 ml of ascorbic acid solution (7.4). *Mix after addition of each reagent.* All reagents must reach room temperature before they are mixed and must be mixed in the order given. If turbidity forms in the combined reagent, shake and let it stand for a few minutes until the turbidity disappears before proceeding. Since the stability of this solution is limited, it must be freshly prepared for each run.

7.6 Sulfuric acid solution, 11 N: Slowly add 310 ml conc. H_2SO_4 to 600 ml distilled water. When cool, dilute to 1 liter.

7.7 Ammonium persulfate.

7.8 Stock phosphorus solution: Dissolve in distilled water 0.2197 g of potassium dihydrogen phosphate, KH_2PO_4, which has been dried in an oven at 105°C. Dilute the solution to 1000 ml; 1.0 ml = 0.05 mg P.

7.9 Standard phosphorus solution: Dilute 10.0 ml of stock phosphorus solution (7.8) to 1000 ml with distilled water; 1.0 ml = 0.5 μg P.

7.9.1 Using standard solution, prepare the following standards in 50.0 ml volumetric flasks:

ml of Standard Phosphorus Solution (7.9)	Conc., mg/1
0	0.00
1.0	0.01
3.0	0.03
5.0	0.05
10.0	0.10
20.0	0.20
30.0	0.30
40.0	0.40
50.0	0.50

7.10 Sodium hydroxide, 1 N: Dissolve 40 g NaOH in 600 ml distilled water. Cool and dilute to 1 liter.

7.11 Phenolphthalein: Dissolve 0.5 g of phenolphthalein in a solution of 50 ml of ethyl or isopropyl alcohol and 50 ml of distilled water.

8. Procedure

8.1 Phosphorus

8.1.1 Add 1 ml of H_2SO_4 solution (7.6) to a 50 ml sample in a 125 ml Erlenmeyer flask.

8.1.2 Add 0.4 g of ammonium persulfate.

8.1.3 Boil gently on a pre-heated hot plate for approximately 30-40 minutes or until a final volume of about 10 ml is reached. Do not allow sample to go to dryness. Alternatively, heat for 30 minutes in an autoclave at 121°C (15-20 psi).

8.14 Adjust the pH of the sample to 7 ±0.2 with 1 N NaOH (7.10) using a pH meter. Cool and dilute the sample to 50 ml. If sample is not clear at this point, filter. CAUTION: Low phosphorus values have been reported because of possible adsorption of phosphorus on iron, aluminum, manganese or other metal precipitates. This can be avoided by filtration before neutralization and redissolving the metal hydroxides that form with 2-3 drops of acid (7.6) before color development.

8.1.5 Determine phosphorus as outlined in (8.3.2 Orthophosphate).

8.2 Hydrolyzable Phosphorus

8.2.1 Add 1 ml of H_2SO_4 solution (7.6) to a 50 ml sample in a 125 ml Erlenmeyer flask.

8.2.2 Boil gently on a pre-heated hot plate for 30-40 minutes or until a final volume of about 10 ml is reached. Do not allow sample to go to dryness. Alternatively, heat for 30 minutes in an autoclave at 121°C (15-20 psi).

8.2.3 Adjust the pH of the sample to 7 ±0.2 with NaOH (7.10) using a pH meter. Cool and dilute the sample to 50 ml.

8.2.4 The sample is now ready for determination of phosphorus as outlined in (8.3.2 Orthophosphate).

8.3 Orthophosphate

8.3.1 Add 1 drop of phenolphthalein indicator (7.11) to the 50.0 ml sample. If a red color develops, add strong-acid solution drop-wise to just discharge the color.

NOTE: If just orthophosphate is being measured, i.e., and there has been no pretreatment of the sample and no subsequent neutralization as outlined above, the pH of the sample must be adjusted to 7±0.2 using a pH meter.

8.3.2 Add 8.0 ml of combined reagent (7.5) to sample and mix thoroughly. After a minimum of ten minutes, but no longer than thirty minutes, measure the color absorbance of each sample at 650 or 880 nm with a spectrophotometer, using the reagent blank as the reference solution.

9. Calculation

9.1 Prepare a standard curve by plotting the absorbance values of standards versus the corresponding phosphorus concentrations.

9.1.1 Process standards and blank exactly as the samples. Run at least a blank and two standards with each series of samples. If the standards do not agree within ±2% of the true value, prepare a new calibration curve.

9.2 Obtain concentration value of sample directly from prepared standard curve. Report results as P, mg/l.

10. Precision and Accuracy

10.1 Thirty-three analysts in nineteen laboratories analyzed natural water samples containing exact increments of organic phosphate, with the following results:

Increment as Total Phosphorus mg P/liter	Precision as Standard Deviation mg P/liter	Accuracy as	
		Bias, %	Bias mg P/liter
0.110	0.033	+ 3.09	+0.003
0.132	0.051	+11.99	+0.016
0.772	0.130	+ 2.96	+0.023
0.882	0.128	− 0.92	−0.008

(FWPCA Method Study 2, Nutrient Analyses)

10.2 Twenty-six analysts in sixteen laboratories analyzed natural water samples containing exact increments of *orthophosphate*, with the following results:

Increment as Orthophosphate mg P/liter	Precision as Standard Deviation mg P/liter	Accuracy as	
		Bias, %	Bias, mg P/liter
0.029	0.010	−4.95	−0.001
0.038	0.008	−6.00	−0.002
0.335	0.018	−2.75	−0.009
0.383	0.023	−1.76	−0.007

(FWPCA Method Study 2, Nutrient Analyses)

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1. Murphy, J., and Riley, J., "A Modified Single Solution for the Determination of Phosphate in Natural Waters." Anal. Chim. Acta., *27*, 31 (1962).

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PHOSPHORUS, ALL FORMS

(Automated Colorimetric Ascorbic Acid Reduction Method)

STORET NO. See Section 4

1. Scope and Application

   1.1 These methods cover the determination of specified forms of phosphorus in drinking, surface, and saline waters, domestic and industrial wastes. They may be applicable to sediment-type samples, sludges, algal blooms, etc., but sufficient data is not available at this time to warrant such usage when measurements for phosphorus content are required.

   1.2 The methods are based on reactions that are specific for the orthophosphate ion. Thus, depending on the prescribed pre-treatment of the sample, the various forms of phosphorus given in Figure 1 may be determined. These forms are, in turn, defined in Section 4.

      1.2.1 Except for in-depth and detailed studies, the most commonly measured forms are phosphorus and dissolved phosphorus, and orthophosphate and dissolved orthophosphate. Hydrolyzable phosphorus is normally found only in sewage-type samples and insoluble forms of phosphorus, as noted, are determined by calculation.

   1.3 The methods are usable in the 0.001 to 1.0 mg P/l range. Approximately 20-30 samples per hour can be analyzed.

2. Summary of Method

   2.1 Ammonium molybdate and antimony potassium tartrate react in an acid medium with dilute solutions of phosphorus to form an antimony-phospho-molybdate complex. This complex is reduced to an intensely blue-colored complex by ascorbic acid. The color is proportional to the phosphorus concentration.

   2.2 Only orthophosphate forms a blue color in this test. Polyphosphates (and some organic phosphorus compounds) may be converted to the orthophosphate form by manual sulfuric-acid-hydrolysis. Organic phosphorus compounds may be converted to the orthophosphate form by manual persulfate digestion(2). The developed color is measured automatically on the AutoAnalyzer.

3. Sample Handling and Preservation

   3.1 If benthic deposits are present in the area being sampled, great care should be taken not to include these deposits.

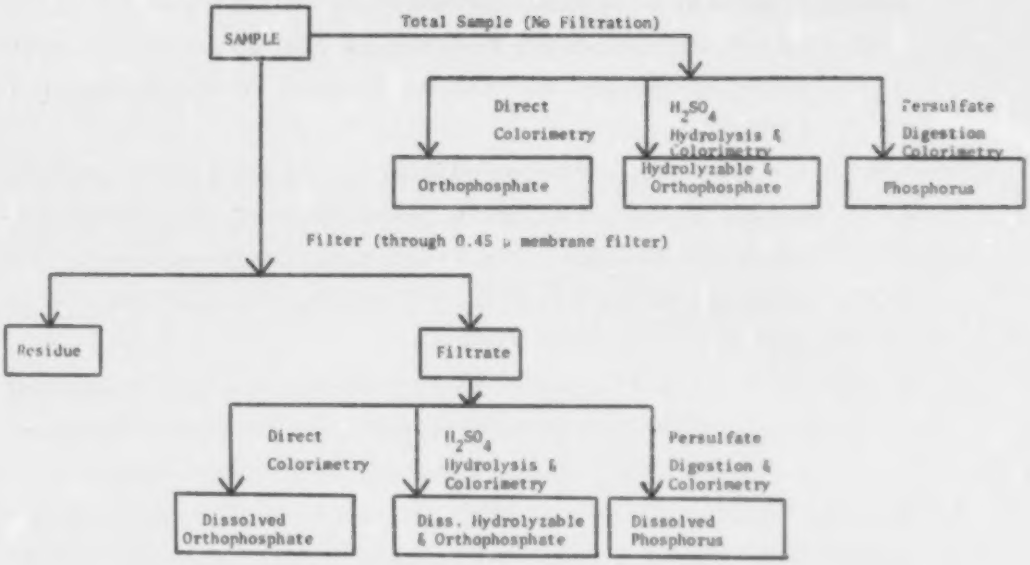
SAMPLE
Total Sample (No Filtration)
Direct
Colorimetry
H_2SO_4
Hydrolysis &
Colorimetry
Persulfate
Digestion
Colorimetry
Orthophosphate
Hydrolyzable &
Orthophosphate
Phosphorus
Filter (through 0.45 μ membrane filter)
Residue
Filtrate
Direct
Colorimetry
H_2SO_4
Hydrolysis &
Colorimetry
Persulfate
Digestion &
Colorimetry
Dissolved
Orthophosphate
Diss. Hydrolyzable
& Orthophosphate
Dissolved
Phosphorus

FIGURE 1. ANALYTICAL SCHEME FOR DIFFERENTIATION OF PHOSPHORUS FORMS

3.2 Sample containers may be of plastic material, such as cubitainers, or of Pyrex glass.

3.3 If the analysis cannot be performed the same day of collection, the sample should be preserved by the addition of 2 ml conc. H_2SO_4 or 40 mg $HgCl_2$ per liter and refrigeration at 4°C. Note $HgCl_2$ interference under (5.4).

4. Definitions and Storet Numbers

4.1 Total Phosphorus (P) – all of the phosphorus present in the sample regardless of form, as measured by the persulfate digestion procedure. (00665)

4.1.1 Total Orthophosphate (P-ortho)–inorganic phosphorus $[(PO_4)^{-3}]$ in the sample as measured by the direct colorimetric analysis procedure. (70507)

4.1.2 Total Hydrolyzable Phosphorus (P-hydro)–phosphorus in the sample as measured by the sulfuric acid hydrolysis procedure, and minus predetermined orthophosphates. This hydrolyzable phosphorus includes polyphosphates $[(P_2O_7)^{-4}$, $(P_3O_{10})^{-5}$, etc.] + some organic phosphorus. (00669)

4.1.3 Total Organic Phosphorus (P-org)–phosphorus (inorganic + oxidizable organic) in the sample as measured by the persulfate digestion procedure, and minus hydrolyzable phosphorus and orthophosphate. (00670)

4.2 Dissolved Phosphorus (P–D) – all of the phosphorus present in the filtrate of a sample filtered through a phosphorus-free filter of 0.45 micron pore size and measured by the persulfate digestion procedure. (00666)

4.2.1 Dissolved Orthophosphate (P–D, ortho) – as measured by the direct colorimetric analysis procedure. (00671)

4.2.2 Dissolved Hydrolyzable Phosphorus (P–D, hydro) – as measured by the sulfuric acid hydrolysis procedure and minus predetermined dissolved orthophosphates. (00672)

4.2.3 Dissolved Organic Phosphorus (P–D, org) – as measured by the persulfate digestion procedure, and minus dissolved hydrolyzable phosphorus and orthophosphate. (00673)

4.3 The following forms, when sufficient amounts of phosphorus are present in the sample to warrant such consideration, may be calculated:

4.3.1 Insoluble Phosphorus (P–I) = (P) – (P–D). (00667)

4.3.1.1 Insoluble orthophosphate (P–I, ortho) = (P, ortho) – (P–D, ortho). (00674)

4.3.1.2 Insoluble Hydrolyzable Phosphorus (P–I, hydro) = (P, hydro) – (P–D, hydro). (00675)

4.3.1.3 Insoluble Organic Phosphorus (P–I, org) = (P, org) – (P–D, org). (00676)

4.4 All phosphorus forms shall be reported as P, mg/l, to the third place.

5. Interferences

5.1 It is reported that no interference is caused by copper, iron, or silicate at concentrations many times greater than their reported concentration in sea water. However, high iron concentrations can cause precipitation of and subsequent loss of phosphorus.

5.2 The salt error for samples ranging from 5 to 20% salt content was found to be less than 1%.

5.3 Arsenate is determined similarly to phosphorus and should be considered when present in concentrations higher than phosphorus. However, at concentrations found in sea water, it does not interfere.

5.4 Mercury chloride, used as a preservative, interferes. This interference is overcome in the AAI method by substituting a solution of sodium chloride (2.5 g/l) in place of the distilled water.

5.5 Sample turbidity must be removed by filtration prior to analysis for orthophosphate. Samples for total or total hydrolyzable phosphorus should be filtered only after digestion. Sample color that absorbs in the photometric range used for analysis will also interfere.

6. Apparatus

6.1 Technicon AutoAnalyzer consisting of:

6.1.1 Sampler.

6.1.2 Manifold (AAI) or Analytical Cartridge (AAII).

6.1.3 Proportioning pump.

6.1.4 Heating bath, 50°C.

6.1.5 Colorimeter equipped with 15 or 50 mm tubular flow cell.

6.1.6 650-660 or 880 nm filter.

6.1.7 Recorder.

6.1.8 Digital printer for AAII (optional).

6.2 Hot plate or autoclave.

6.3 Acid-washed glassware: All glassware used in the determination should be washed with hot 1:1 HCl and rinsed with distilled water. The acid-washed glassware should be filled with distilled water and treated with all the reagents to remove the last traces of phosphorus that might be adsorbed on the glassware. Preferably, this glassware should be used only for the determination of phosphorus and after use it should be rinsed with distilled water and kept covered until needed again. If this is done, the treatment with 1:1 HCl and reagents is only required occasionally. *Commercial detergents should never be used.*

7. Reagents

7.1 Sulfuric acid solution, 5N: Slowly add 70 ml of conc. H_2SO_4 to approximately 400 ml of distilled water. Cool to room temperature and dilute to 500 ml with distilled water.

7.2 Antimony potassium tartrate solution: Weigh 0.3 g $K(SbO)C_4H_4O_6 \cdot 1/2H_2O$, dissolve in 50 ml distilled water in 100 ml volumetric flask, dilute to volume. Store at 4°C in a dark, glass-stoppered bottle.

7.3 Ammonium molybdate solution: Dissolve 4 g $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ in 100 ml distilled water. Store in a plastic bottle at 4°C.

7.4 Ascorbic acid, 0.1M: Dissolve 1.8 g of ascorbic acid in 100 ml of distilled water. The solution is stable for about a week if prepared with water containing no more than trace amounts of heavy metals and stored at 4°C.

7.5 Combined reagent (AAI): Mix the above reagents in the following proportions for 100 ml of the mixed reagent: 50 ml of 5N H_2SO_4 (7.1), 5 ml of antimony potassium tartrate solution (7.2), 15 ml of ammonium molybdate solution (7.3), and 30 ml of ascorbic acid solution (7.4). *Mix after addition of each reagent.* All reagents must reach room temperature before they are mixed and must be mixed in the order given. If turbidity forms in the combined reagent, shake and let it stand for a few minutes until the turbidity disappears before processing. This volume is sufficient for 4 hours operation. Since the stability of this solution is limited, it must be freshly prepared for each run.

NOTE 1: A stable solution can be prepared by not including the ascorbic acid in the combined reagent. If this is done, the mixed reagent (molybdate, tartrate, and acid) is pumped through the distilled water line and the ascorbic acid solution (30 ml of 7.4 diluted to 100 ml with distilled water) through the original mixed reagent line.

7.6 Sulfuric acid solution, 11 N: Slowly add 310 ml conc. H_2SO_4 to 600 ml distilled water. When cool, dilute to 1 liter.

7.7 Ammonium persulfate.

7.8 Acid wash water: Add 40 ml of sulfuric acid solution (7.6) to 1 liter of distilled water and dilute to 2 liters. (Not to be used when only orthophosphate is being determined).

7.9 Phenolphthalein indicator solution (5 g/l): Dissolve 0.5 g of phenolphthalein in a solution of 50 ml of ethyl or isopropyl alcohol and 50 ml of distilled water.

7.10 Stock phosphorus solution: Dissolve 0.4393 g of pre-dried (105°C for 1 hour) KH_2PO_4 in distilled water and dilute to 1000 ml. 1.0 ml = 0.1 mg P.

7.11 Standard phosphorus solution: Dilute 100.0 ml of stock solution (7.10) to 1000 ml with distilled water. 1.0 ml = 0.01 mg P.

7.12 Standard phosphorus solution: Dilute 100.0 ml of standard solution (7.11) to 1000 ml with distilled water. 1.0 ml = 0.001 mg P.

7.13 Prepare a series of standards by diluting suitable volumes of standard solutions (7.11) and (7.12) to 100.0 ml with distilled water. The following dilutions are suggested:

ml of Standard Phosphorus Solution (7.12)	Conc., mg P/l
0.0	0.00
2.0	0.02
5.0	0.05
10.0	0.10
ml of Standard Phosphorus Solution (7.11)	
2.0	0.20
5.0	0.50
8.0	0.80
10.0	1.00

8. Procedure

8.1 Phosphorus

8.1.1 Add 1 ml of sulfuric acid solution (7.6) to a 50 ml sample and standards in a 125 ml Erlenmeyer flask.

8.1.2 Add 0.4 g of ammonium persulfate.

8.1.3 Boil gently on a pre-heated hot plate for approximately 30-40 minutes or until a final volume of about 10 ml is reached. Do not allow sample to go to dryness. Alternately, heat for 30 minutes in an autoclave at 121°C (15-20 psi).

8.1.4 Cool and dilute the sample to 50 ml. If sample is not clear at this point, filter.

8.1.5 Determine phosphorus as outlined in (8.3.2) with acid wash water (7.8) in wash tubes.

8.2 Hydrolyzable Phosphorus

8.2.1 Add 1 ml of sulfuric acid solution (7.6) to a 50 ml sample and standards in a 125 ml Erlenmeyer flask.

8.2.2 Boil gently on a pre-heated hot plate for 30-40 minutes or until a final volume of about 10 ml is reached. Do not allow sample to go to dryness. Alternatively, heat for 30 minutes in an autoclave at 121°C (15-20 psi).

8.2.3 Cool and dilute the sample to 50 ml. If sample is not clear at this point, filter.

8.2.4 Determine phosphorus as outlined in (8.3.2) with acid wash water (7.8) in wash tubes.

8.3 Orthophosphate

8.3.1 Add 1 drop of phenolphthalein indicator solution (7.9) to approximately 50 ml of sample. If a red color develops, add sulfuric acid solution (7.6) drop-wise to just discharge the color. Acid samples must be neutralized with 1 N sodium hydroxide (40 g NaOH/l).

8.3.2 Set up manifold as shown in Figure 2, AAI or Figure 3, AAII.

8.3.3 Allow both colorimeter and recorder to warm up for 30 minutes. Obtain a stable baseline with all reagents, feeding distilled water through the sample line.

8.3.4 For the AAI system, sample at a rate of 20/hr, 1 minute sample, 2 minute wash. For the AAII system, use a 30/hr, 2:1 cam, and a common wash.

8.3.5 Place standards in Sampler in order of decreasing concentration. Complete filling of sampler tray with unknown samples.

8.3.6 Switch sample line from distilled water to Sampler and begin analysis.

9. Calculation

9.1 Prepare a standard curve by plotting peak heights of processed standards against known concentrations. Compute concentrations of samples by comparing sample peak heights with standard curve. Any sample whose computed value is less than

5% of its immediate predecessor must be rerun.

10. Precision and Accuracy (AAI system)

10.1 Six laboratories analyzed four natural water samples containing exact increments of orthophosphate, with the following results:

Increment as Orthophosphate mg P/liter	Precision as Standard Deviation mg P/liter	Accuracy as	
		Bias, %	Bias, mg P/liter
0.04	0.019	+16.7	+0.007
0.04	0.014	− 8.3	−0.003
0.29	0.087	−15.5	−0.05
0.30	0.066	−12.8	−0.04

(FWPCA Method Study 4, Automated Methods – In preparation).

10.2 In a single laboratory, (MDQARL), using surface water samples at concentrations of 0.04, 0.19, 0.35, and 0.84 mg P/l, standard deviations were ±0.005, ±0.000, ±0.003, and ±0.000, respectively.

10.3 In a single laboratory, (MDQARL), using surface water samples at concentrations of 0.07 and 0.76 mg P/l, recoveries were 99% and 100%, respectively.

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4. ASTM Standards, Part 23, Water; Atmospheric Analysis, 515-72, p 388 (1973).

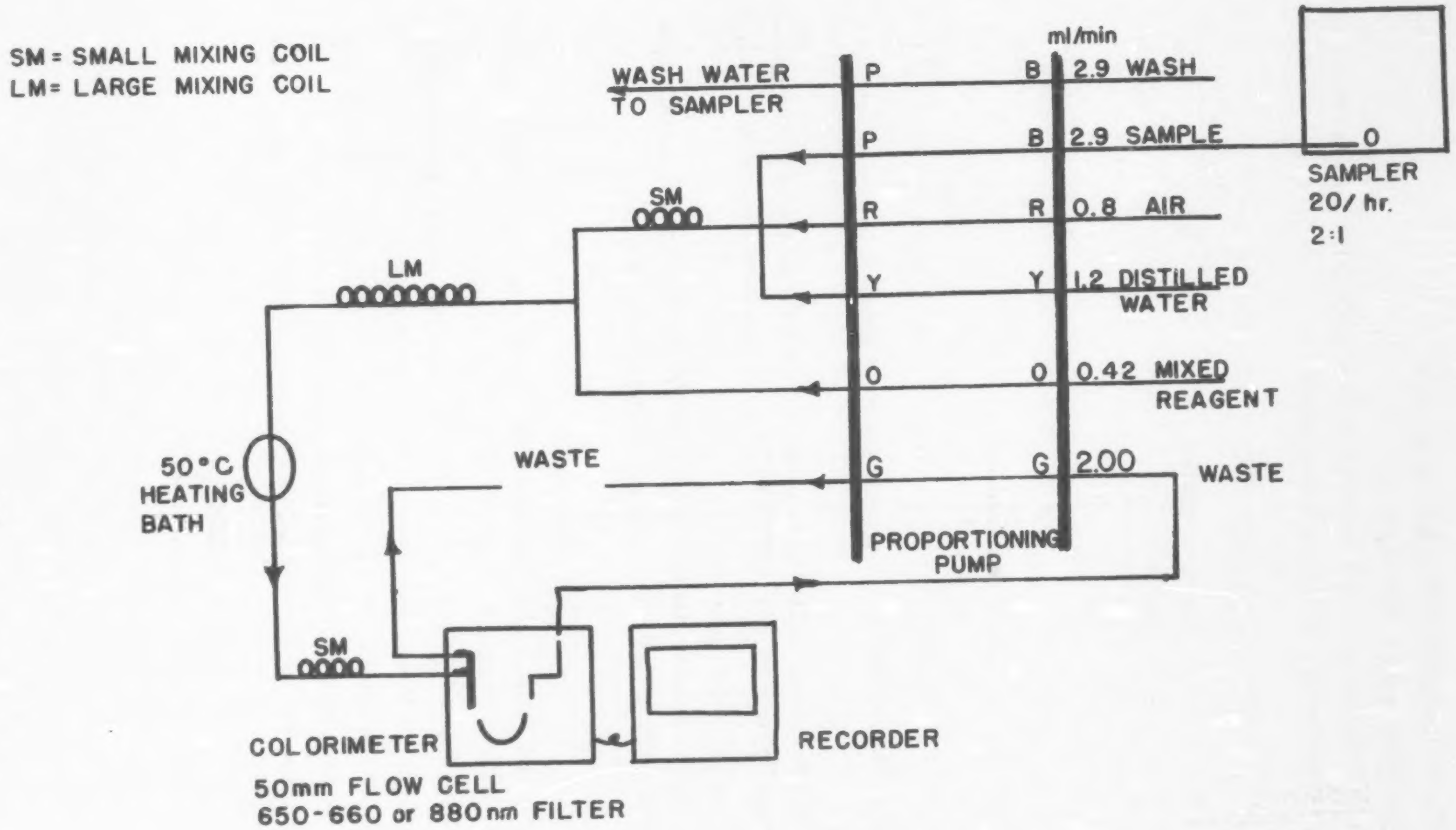
SM = SMALL MIXING COIL
LM = LARGE MIXING COIL
ml/min
WASH WATER
TO SAMPLER
P
P
R
Y
O
G
B
B
R
Y
O
G
2.9 WASH
2.9 SAMPLE
0.8 AIR
1.2 DISTILLED WATER
0.42 MIXED REAGENT
2.00
WASTE
O
SAMPLER
20/ hr.
2:1
SM
LM
50 °C
HEATING
BATH
WASTE
PROPORTIONING
PUMP
SM
COLORIMETER
50mm FLOW CELL
650-660 or 880nm FILTER
RECORDER

FIGURE 2 PHOSPHORUS MANIFOLD AA I

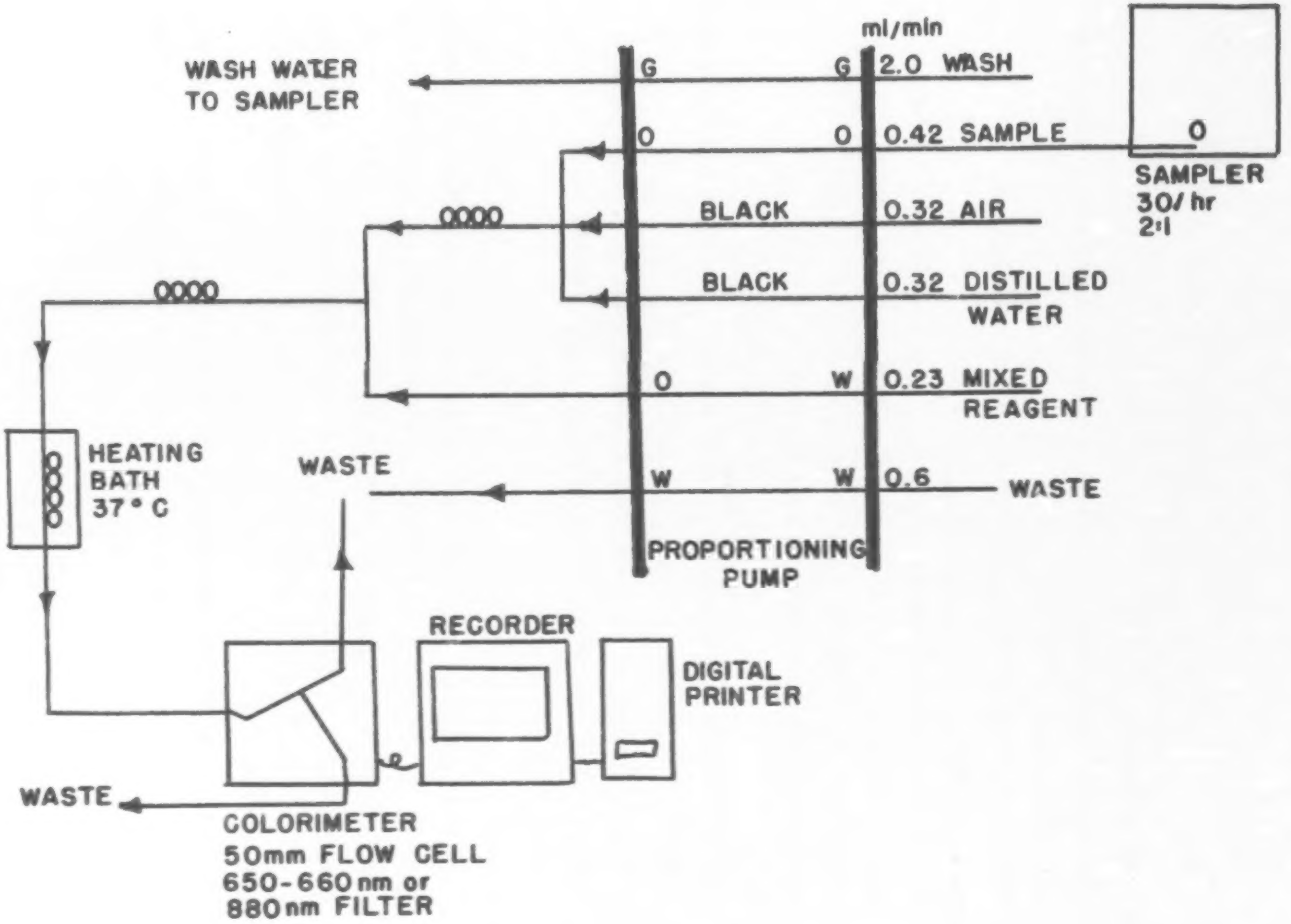
ml/min
WASH WATER
TO SAMPLER
G
G
2.0 WASH
O
O
0.42 SAMPLE
O
SAMPLER
30/ hr
2:1
BLACK
0.32 AIR
BLACK
0.32 DISTILLED
WATER
O
W
0.23 MIXED
REAGENT
W
W
0.6
WASTE
WASTE
PROPORTIONING
PUMP
HEATING
BATH
37 ° C
RECORDER
DIGITAL
PRINTER
WASTE
COLORIMETER
50mm FLOW CELL
650-660 nm or
880 nm FILTER

FIGURE 3 PHOSPHORUS MANIFOLD AA II

RESIDUE, Total Filterable
(Dried at 180°C)

STORET NO. 70300

1. Scope and Application
   1.1 This method is applicable to drinking, surface, and saline waters, domestic and industrial wastes.
   1.2 The practical range of the determination is 10 mg/l to 20,000 mg/l.
2. Summary of Method
   2.1 A well-mixed sample is filtered through a standard glass fiber filter. The filtrate is evaporated and dried to constant weight at 180°C.
   2.2 If Residue, Total Non-Filterable is being determined, the filtrate from that method may be used for Residue, Total Filterable.
3. Definitions
   3.1 Filterable solids are defined as those solids capable of passing through a standard glass fiber filter and dried to constant weight at 180°C.
4. Sample Handling and Preservation
   4.1 Preservation of the sample is not practical; analysis should begin as soon as possible.
5. Interferences
   5.1 Highly mineralized waters containing significant concentrations of calcium, magnesium, chloride and/or sulfate may be hygroscopic and will require prolonged drying, desiccation and rapid weighing.
   5.2 Samples containing high concentrations of bicarbonate will require careful and possibly prolonged drying at 180°C to insure that all the bicarbonate is converted to carbonate.
   5.3 Too much residue in the evaporating dish will crust over and entrap water that will not be driven off during drying. Total residue should be limited to about 200 mg.
6. Apparatus
   6.1 Glass fiber filter discs, 4.7 cm or 2.2 cm, without organic binder, Reeve Angel type 934-AH, Gelman type A/E, or equivalent.
   6.2 Filter holder, membrane filter funnel or Gooch crucible adapter.
   6.3 Suction flask, 500 ml.
   6.4 Gooch crucibles, 25 ml (if 2.2 cm filter is used).

6.5 Evaporating dishes, porcelain, 100 ml volume. (Vycor or platinum dishes may be substituted).

6.6 Steam bath.

6.7 Drying oven, 180°C±2°C.

6.8 Desiccator.

6.9 Analytical balance, 200 g capacity, capable of weighing to 0.1 mg.

7. Procedure

7.1 Preparation of glass fiber filter disc: Place the disc on the membrane filter apparatus or insert into bottom of a suitable Gooch crucible. While vacuum is applied, wash the disc with three successive 20 ml volumes of distilled water. Remove all traces of water by continuing to apply vacuum after water has passed through. Discard washings.

7.2 Preparation of evaporating dishes: Heat the clean dish to 550±50°C for one hour in a muffle furnace. Cool in desiccator and store until needed. Weigh immediately before use.

7.3 Assemble the filtering apparatus and begin suction. Shake the sample vigorously and rapidly transfer 100 ml to the funnel by means of a 100 ml graduated cylinder. If total filterable residue is low, a larger volume may be filtered.

7.4 Filter the sample through the glass fiber filter and continue to apply vacuum for about 3 minutes after filtration is complete to remove as much water as possible.

7.5 Transfer 100 ml (or a larger volume) of the filtrate to a weighed evaporating dish and evaporate to dryness on a steam bath.

7.6 Dry the evaporated sample for at least one hour at 180±2°C. Cool in a desiccator and weigh. Repeat the drying cycle until a constant weight is obtained or until weight loss is less than 0.5 mg.

8. Calculation

8.1 Calculate filterable residue as follows:

$$\text{Filt. residue, mg/l} = \frac{(A-B) \times 1000}{C}$$

where:

A = weight of dried residue + dish in mg

B = weight of dish in mg

C = volume of filtrate used in ml

9. Precision and Accuracy

9.1 Precision data are not available at this time.

9.2 Accuracy data on actual sample cannot be obtained.

RESIDUE, TOTAL NON-FILTERABLE

STORET NO. 00530

1. Scope and Application
   1.1 This method is applicable to drinking, surface, and saline waters, domestic and industrial wastes.
   1.2 The practical range of the determination is 10 mg/l to 20,000 mg/l.
2. Summary of Method
   2.1 A well-mixed sample is filtered through a standard glass fiber filter, and the residue retained on the filter is dried to constant weight at 103-105°C.
   2.2 The filtrate from this method may be used for Residue, Total Filterable.
3. Definitions
   3.1 Non-filterable solids are defined as those solids which are retained by a standard glass fiber filter and dried to constant weight at 103-105°C.
4. Sample Handling and Preservation
   4.1 Non-homogeneous particulates such as leaves, sticks, fish, and lumps of fecal matter should be excluded from the sample.
   4.2 Preservation of the sample is not practical; analysis should begin as soon as possible.
5. Interferences
   5.1 Too much residue on the filter will entrap water and may require prolonged drying.
6. Apparatus
   6.1 Glass fiber filter discs, 4.7 cm or 2.2 cm, without organic binder, Reeve Angel type 934-A or 984-H, Gelman type A/E, or equivalent.
   6.2 Filter holder, membrane filter funnel or Gooch crucible adapter.
   6.3 Suction flask, 500 ml.
   6.4 Gooch crucibles, 25 ml (if 2.2 cm filter is used).
   6.5 Drying oven, 103-105°C.
   6.6 Desiccator.
   6.7 Analytical balance, 200 g capacity, capable of weighing to 0.1 mg.
7. Procedure
   7.1 Preparation of glass fiber filter disc: Place the disc on the membrane filter apparatus or insert into bottom of a suitable Gooch crucible. While vacuum is applied, wash the disc with three successive 20 ml volumes of distilled water.

Remove all traces of water by continuing to apply vacuum after water has passed through. Remove filter from membrane filter apparatus or both crucible and filter if Gooch crucible is used, and dry in an oven at 103-105°C for one hour. Remove to desiccator and store until needed. Weigh immediately before use.

7.2 Assemble the filtering apparatus and begin suction. Shake the sample vigorously and rapidly transfer 100 ml to the funnel by means of a 100 ml volumetric cylinder. If suspended matter is low, a larger volume may be filtered.

7.3 Carefully remove the filter from the membrane filter funnel assembly. Alternatively, remove crucible and filter from crucible adapter. Dry at least one hour at 103-105°C. Cool in a desiccator and weigh. Repeat the drying cycle until a constant weight is obtained or until weight loss is less than 0.5 mg.

8. Calculations

8.1 Calculate non-filterable residue as follows:

$$\text{Non-filt. residue, mg/l} = \frac{(A-B) \times 1000}{C}$$

where:

A = weight of filter + residue in mg

B = weight of filter in mg

C = ml of sample filtered in ml

9. Precision and Accuracy

9.1 Precision data are not available at this time.

9.2 Accuracy data on actual samples cannot be obtained.

RESIDUE, Total

STORET NO. 00500

1. Scope and Application
   - 1.1 This method is applicable to drinking, surface, and saline waters, domestic and industrial wastes.
   - 1.2 The practical range of the determination is from 10 mg/l to 20,000 mg/l.
2. Summary of Method
   - 2.1 A well mixed aliquot of the test sample is quantitatively transferred to a pre-weighed evaporating dish and evaporated to dryness at 103-105°C.
3. Definitions
   - 3.1 Total Residue is defined as the sum of the homogenous suspended and dissolved materials in a sample.
4. Sample Handling and Preservation
   - 4.1 Samples should be analyzed as soon as practicable.
5. Interferences
   - 5.1 Large, floating particles or submerged agglomerates (non-homogenous materials) should be excluded from the test sample.
   - 5.2 Floating oil and grease, if present, should be included in the sample and dispersed by a blender device before aliquoting.
6. Apparatus
   - 6.1 Evaporating dishes, porcelain, 90 mm, 100 ml capacity. (Vycor or platinum dishes may be substituted and smaller size dishes may be used if required.)
7. Procedure
   - 7.1 Heat the clean evaporating dish to 550±50°C for 1 hour in a muffle furnace. Cool, desiccate, weigh and store in desiccator until ready for use.
   - 7.2 Transfer a measured aliquot of sample to the pre-weighed dish and evaporate to dryness on a steam bath or in a drying oven.
     - 7.2.1 Choose an aliquot of sample sufficient to contain a residue of at least 25 mg. To obtain a weighable residue, successive aliquots of sample may be added to the same dish.
     - 7.2.2 If evaporation is performed in a drying oven, the temperature should be lowered to approximately 98°C to prevent boiling and splattering of the sample.
   - 7.3 Dry the evaporated sample for at least 1 hour at 103-105°C. Cool in a desiccator

and weigh. Repeat the cycle of drying at 103-105°C, cooling, desiccating and weighing until a constant weight is obtained or until loss of weight is less than 4% of the previous weight, or 0.5 mg, whichever is less.

8. Calculation

8.1 Calculate total residue as follows:

$$\text{Total residue, mg/l} = \frac{(A-B) \times 1000}{C}$$

where:

A = weight of sample + dish in mg
B = weight of dish in mg
C = volume of sample in ml

9. Precision and Accuracy

9.1 Precision and accuracy data are not available at this time.

RESIDUE, Volatile

STORET NO. Total 00505
Nonfilterable 00535
Filterable 00520

1. Scope and Application

1.1 This method determines the weight of solid material combustible at 550°C.

1.2 The test is useful in obtaining a rough approximation of the amount of organic matter present in the solid fraction of sewage, activated sludge, industrial wastes, or bottom sediments.

2. Summary of Method

2.1 The residue obtained from the determination of total, filterable or non-filterable residue is ignited at 550°C in a muffle furnace. The loss of weight on ignition is reported as mg/l volatile residue.

3. Comments

3.1 The test is subject to many errors due to loss of water of crystallization, loss of volatile organic matter prior to combustion, incomplete oxidation of certain complex organics, and decomposition of mineral salts during combustion.

3.2 The results should not be considered an accurate measure of organic carbon in the sample, but may be useful in the control of plant operations.

3.3 The principal source of error in the determination is failure to obtain a representative sample.

4. Sample Handling and Preservation

4.1 Preservation of the sample is not practical; analysis should begin as soon as possible.

5. Precision and Accuracy

5.1 A collaborative study involving three laboratories examining four samples by means of ten replicates showed a standard deviation of ±11 mg/l at 170 mg/l volatile residue concentration.

6. Reference

6.1 The procedure to be used for this determination is found in:
Standard Methods for the Examination of Water and Wastewater, 13th Edition, p 536, Method 224B (1971).

SETTLEABLE MATTER

STORET NO. 50086

1. Scope and Application

   1.1 This method is applicable to surface and saline waters, domestic and industrial wastes.

   1.2 The practical lower limit of the determination is about 1 ml/l/hr.

2. Summary of Method

   2.1 Settleable matter is measured volumetrically with an Imhoff cone.

3. Comments

   3.1 For some samples, a separation of settleable and floating materials will occur; in such cases the floating materials are not measured.

   3.2 Many treatment plants, especially plants equipped to perform gravimetric measurements, determine residue non-filterable (suspended solids), in preference to settleable matter, to insure that floating matter is included in the analysis.

4. Precision and Accuracy

   4.1 Data on this determination is not available at this time.

5. References

   5.1 The procedure to be used for this determination is found in:
   Standard Methods for the Examination of Water and Wastewater, 13th Edition, p 539, Method 224F, Procedure a (1971).

SILICA, Dissolved

STORET NO. 00955

1. Scope and Application
   1.1 This method is applicable to drinking, surface, and saline waters, domestic and industrial wastes.
   1.2 The working range of the method is approximately 2 to 25 mg silica/l. The upper range can be extended by taking suitable aliquots; the lower range can be extended by the addition of amino-naphthol-sulfonic acid solution, as described in the ASTM reference.
2. Summary of Method
   2.1 A well-mixed sample is filtered through a 0.45 μ membrane filter. The filtrate, upon the addition of molybdate ion in acidic solution, forms a greenish-yellow color complex proportional to the dissolved silica in the sample. The color complex is then measured spectrophotometrically.
3. Comments
   3.1 Excessive color and/or turbidity interfere. Correct by running blanks prepared without addition of the ammonium molybdate solution.
4. Precision and Accuracy
   4.1 Photometric evaluations by the amino-naphthol-sulfonic acid procedure have an estimated precision of ±0.10 mg/l in the range from 0 to 2 mg/l (ASTM).
   4.2 Photometric evaluations of the silico-molybdate color in the range from 2 to 50 mg/l have an estimated precision of approximately 4% of the quantity of silica measured (ASTM).
5. Reference
   5.1 The procedure to be used for this determination is found in:
   Standard Methods for the Examination of Water and Wastewater, 13th Edition, p 303, Method 151B (1971).
   ASTM Standards, Part 23, Water; Atmospheric Analysis, p 401, Method D859-68 (1973).

SPECIFIC CONDUCTANCE

(μmhos at 25°C)

STORET NO. 00095

1. Scope and Application
   1.1 This method is applicable to drinking, surface, and saline waters, domestic and industrial wastes.
2. Summary of Method
   2.1 The specific conductance of a sample is measured by use of a self-contained conductivity meter, Wheatstone bridge-type, or equivalent.
   2.2 Samples are preferably analyzed at 25°C. If not, temperature corrections are made and results reported at 25°C.
3. Comments
   3.1 Instrument must be standardized with KCl solution before daily use.
   3.2 Conductivity cell must be kept clean.
   3.3 Field measurements with comparable instruments are reliable.
4. Precision and Accuracy
   4.1 Forty-one analysts in 17 laboratories analyzed six synthetic water samples containing increments of inorganic salts, with the following results:

Increment as Specific Conductance μmhos/cm	Precision as Standard Deviation μmhos/cm	Accuracy as	
		Bias, %	Bias, μmhos/cm
100	7.55	–2.02	–2.0
106	8.14	–0.76	–0.8
808	66.1	–3.63	–29.3
848	79.6	–4.54	–38.5
1640	106	–5.36	–87.9
1710	119	–5.08	–86.9

(FWPCA Method Study 1, Mineral and Physical Analyses.)

   4.2 In a single laboratory (MDQARL), using surface water samples with an average conductivity of 536 μmhos/cm at 25°C, the standard deviation was ±6.

5. References

5.1 The procedure to be used for this determination is found in:

Standard Methods for the Examination of Water and Wastewater, 13th Edition, p 323, Method 154 (1971).

ASTM Standards, Part 23, Water; Atmospheric Analysis, p 128, Method D1125-64 (1973).

SULFATE

(Turbidimetric)

STORET NO. 00945

1. Scope and Application

    1.1 This method is applicable to drinking and surface waters, domestic and industrial wastes.

    1.2 The method is suitable for all concentration ranges of sulfate; however, in order to obtain reliable readings, use a sample aliquot containing not more than 40 mg SO_4/l.

2. Summary of Method

    2.1 Sulfate ion is converted to a barium sulfate suspension under controlled conditions. The resulting turbidity is determined by a colorimeter or spectrophotometer and compared to a curve prepared from standard sulfate solutions.

    2.2 Suspended matter and color interfere. Correct by running blanks from which the barium chloride has been omitted.

3. Comments

    3.1 Proprietary reagents, such as Hach Sulfaver or equivalent, are acceptable.

4. Precision and Accuracy

    4.1 Thirty-four analysts in 16 laboratories analyzed six synthetic water samples containing exact increments of inorganic sulfate with the following results:

Increment as Sulfate mg/liter	Precision as Standard Deviation mg/liter	Accuracy as	
		Bias, %	Bias, mg/liter
8.6	2.30	–3.72	–0.3
9.2	1.78	–8.26	–0.8
110	7.86	–3.01	–3.3
122	7.50	–3.37	–4.1
188	9.58	+0.04	+0.1
199	11.8	–1.70	–3.4

(FWPCA Method Study 1, Mineral and Physical Analyses).

5. References

5.1 The procedure to be used for this determination is found in:

Standard Methods for the Examination of Water and Wastewater, 13th Edition, p 334, Method 156C (1971).

ASTM Standards, Part 23, Water; Atmospheric Analysis, p 425, Method B, D516-68 (1973).

SULFATE

(Automated Chloranilate Method)

STORET NO. 00945

1. Scope and Application
   1.1 This automated method is applicable to drinking and surface waters, domestic and industrial wastes, in the range of 10 to 400 mg SO_4/l. Approximately 15 samples per hour can be analyzed.
2. Summary of Method
   2.1 When solid barium chloranilate is added to a solution containing sulfate, barium sulfate is precipitated, releasing the highly colored acid chloranilate ion. The color intensity in the resulting chloranilic acid is proportional to the amount of sulfate present.
3. Sample Handling and Preservation
   3.1 No special requirements.
4. Interferences
   4.1 Cations, such as calcium, aluminum, and iron, interfere by precipitating the chloranilate. These ions are removed automatically by passage through an ion exchange column.
5. Apparatus
   5.1 Technicon AutoAnalyzer consisting of:
      5.1.1 Sampler I.
      5.1.2 Continuous filter.
      5.1.3 Manifold.
      5.1.4 Proportioning pump.
      5.1.5 Colorimeter equipped with 15 mm tubular flow cell and 520 nm filters.
      5.1.6 Recorder.
      5.1.7 Heating bath, 45°C.
   5.2 Magnetic stirrer.
6. Reagents
   6.1 Barium chloranilate: Add 9 g of barium chloranilate ($BaC_6Cl_2O_4$) to 333 ml of ethyl alcohol and dilute to 1 liter with distilled water.
   6.2 Acetate buffer, pH 4.63: Dissolve 13.6 g of sodium acetate in distilled water. Add 6.4 ml of acetic acid and dilute to 1 liter with distilled water. Make fresh weekly.

6.3 NaOH-EDTA solution: Dissolve 65 g of NaOH and 6 g of EDTA in distilled water and dilute to 1 liter.

NOTE 1: This solution is also used to clean out manifold system at end of sampling run.

6.4 Ion exchange resin: Dowex-50 W-X8, ionic form – H+.

NOTE 2: Column is prepared by sucking a slurry of the resin into 12 inches of 3/16-inch OD sleeving. This may be conveniently done by using a pipette and a loose-fitting glass wool plug in the sleeve. The column, upon exhaustion, turns red.

6.5 Stock solution: Dissolve 1.4790 g of oven-dried (105°C) Na_2SO_4 in distilled water and dilute to 1 liter in a volumetric flask. 1.0 ml = 1.0 mg.

6.5.1 Prepare a series of standards by diluting suitable volumes of stock solution to 100.0 ml with distilled water. The following dilutions are suggested:

ml of Stock Solution	Conc., mg/l
1.0	10
2.0	20
4.0	40
6.0	60
8.0	80
10.0	100
15.0	150
20.0	200
30.0	300
40.0	400

7. Procedure

7.1 Set up manifold as shown in Figure 1. (Note that any precipitated $BaSO_4$ and the unused barium chloranilate are removed by filtration. If any $BaSO_4$ should come through the filter, it is complexed by the NaOH–EDTA reagent).

7.2 Allow both colorimeter and recorder to warm up for 30 minutes. Run a baseline with all reagents, feeding distilled water through the sample line. Adjust dark current and operative opening on colorimeter to obtain suitable baseline.

7.3 Place distilled water wash tubes in alternate openings in sampler and set sample timing at 2.0 minutes.

7.4 Place working standards in sampler in order of decreasing concentration. Complete filling of sampler tray with unknown samples.

7.5 Switch sample line from distilled water to sampler and begin analysis.

8. Calculation

8.1 Prepare standard curve by plotting peak heights of processed standards against known concentrations. Compute concentration of samples by comparing sample peak heights with standard curve.

9. Precision and Accuracy

9.1 In a single laboratory (MDQARL), using surface water samples at concentrations of 39, 111, 188 and 294 mg SO_4/l, the standard deviations were ±0.6, ±1.0, ±2.2 and ±0.8, respectively.

9.2 In a single laboratory (MDQARL) using surface water samples at concentrations of 82 and 295 mg SO_4/l, recoveries were 99% and 102%, respectively.

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1. Barney, J. E., and Bertolocini, R. J., Anal. Chem., *29*, 283 (1957).
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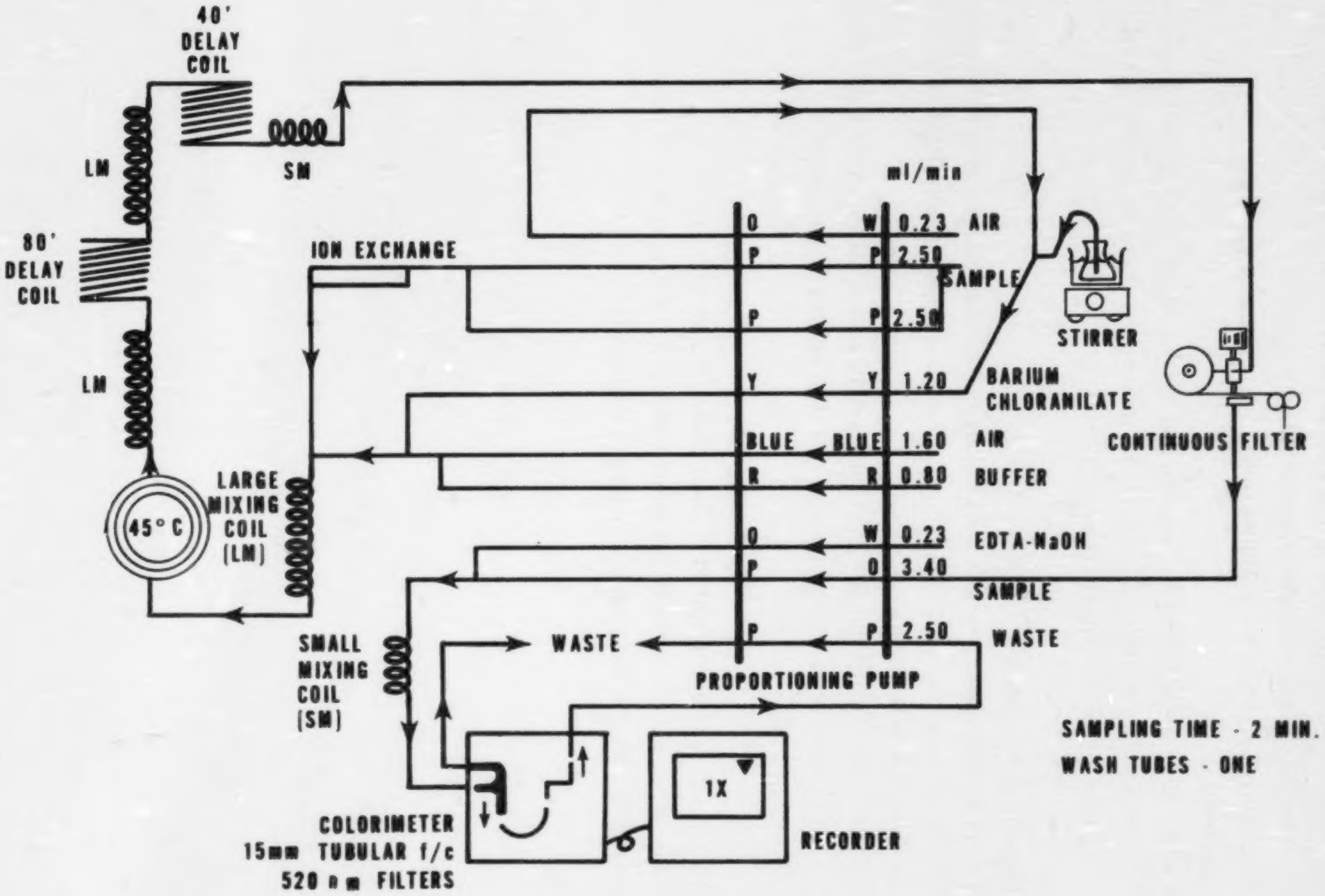
40' DELAY COIL
SM
LM
80' DELAY COIL
LM
45° C
LARGE MIXING COIL (LM)
ION EXCHANGE
ml/min
O
W 0.23 AIR
P
P 2.50
SAMPLE
P
P 2.50
STIRRER
Y
Y 1.20
BARIUM CHLORANILATE
CONTINUOUS FILTER
BLUE
BLUE 1.60 AIR
R
R 0.80 BUFFER
O
W 0.23 EDTA-NaOH
P
O 3.40
SAMPLE
P
P 2.50 WASTE
WASTE
PROPORTIONING PUMP
SMALL MIXING COIL (SM)
1X
COLORIMETER 15mm TUBULAR f/c 520 nm FILTERS
RECORDER
SAMPLING TIME - 2 MIN.
WASH TUBES - ONE

FIGURE 1 - SULFATE MANIFOLD AA-I

SULFATE

(Gravimetric)

STORET NO. 00945

1. Scope and Application

   1.1 This method is applicable to drinking, surface, and saline waters, domestic and industrial wastes.

   1.2 This method is the most accurate method for sulfate concentrations above 10 mg/l. Therefore, it should be used whenever results of the greatest accuracy are required.

2. Summary of Method

   2.1 Sulfate is precipitated as barium sulfate in a hydrochloric acid medium by the addition of barium chloride. After a period of digestion, the precipitate is filtered, washed with hot water until free of chloride, ignited, and weighed as $BaSO_4$.

3. Comments

   3.1 High results may be obtained for samples that contain suspended matter, nitrate, sulfite and silica.

   3.2 Alkali metal sulfates frequently yield low results. This is especially true of alkali hydrogen sulfates. Occlusion of alkali sulfate with barium sulfate causes the substitution of an element of lower atomic weight than barium in the precipitate. Hydrogen sulfate of alkali metal acts similarly and decomposes when heated. Heavy metals such as chromium and iron, cause low results by interfering with complete precipitation and by formation of heavy metal sulfates.

4. Precision and Accuracy

   4.1 A synthetic unknown sample containing 259 mg/l sulfate, 108 mg/l Ca, 82 mg/l Mg, 3.1 mg/l K, 19.9 mg/l Na, 241 mg/l chloride, 250 μg/l nitrite N, 1.1 mg/l nitrate N and 42.5 mg/l total alkalinity (contributed by $NaHCO_3$), was analyzed by the gravimetric method, with a relative standard deviation of 4.7% and a relative error of 1.9% in 32 laboratories.

5. Reference

   5.1 The procedure to be used for this determination is found in:

   Standard Methods for the Examination of Water and Wastewater, 13th Edition, p 331, Method 156 A (1971).

   ASTM Standards, Part 23, Water; Atmospheric Analysis, p 425, Method A, D516-68 (1973).

SULFIDE

(Titrimetric Iodine Method)

STORET NO. Total 00745
Dissolved 00746

1. Scope and Application
   1.1 This method is applicable to the measurement of total and dissolved sulfides in drinking, surface, and saline waters, domestic and industrial wastes.
   1.2 Acid insoluble sulfides are not measured by the use of this test. (Copper sulfide is the only common sulfide in this class).
   1.3 This method is suitable for the measurement of sulfide in concentrations above 1 mg/l.
2. Summary of Method
   2.1 Sulfides are stripped from the acidified sample with an inert gas and collected in a zinc acetate solution. Excess iodine added to the zinc sulfide suspension reacts with the sulfide under acidic conditions. Thiosulfate is used to measure unreacted iodine to indicate the quantity of iodine consumed by sulfide.
3. Comments
   3.1 Reduced sulfur compounds, such as sulfite, thiosulfate and hydrosulfite, which decompose in acid may yield erratic results. Also, volatile iodine-consuming substances will give high results.
   3.2 Samples must be taken with a minimum of aeration. Sulfide may be volatilized by aeration and any oxygen inadvertently added to the sample may convert the sulfide to an unmeasurable form.
   3.3 If the sample is not preserved with zinc acetate, the analysis must be started immediately. Similarly, the measurement of dissolved sulfides must also be commenced immediately.
4. Precision and Accuracy
   4.1 Precision and accuracy for this method have not been determined.
5. References
   5.1 The procedure to be used for this determination is found in:
   Standard Methods for the Examination of Water and Wastewaters, 13th Edition, p 551-555, Method No. 228A (1971).

SULFITE

STORET NO. 00740

1. Scope and Application
   1.1 This method is applicable to drinking and surface waters, sewage and industrial wastes.
   1.2 The minimum detectable limit is 2-3 mg/l SO_3.
2. Summary of Method
   2.1 An acidified sample containing an indicator is titrated with a standard potassium iodide-iodate titrant to a faint permanent blue end point.
3. Comments
   3.1 The temperature of the sample must be below 50°C.
   3.2 Care must be taken to allow as little contact with air as possible. For example, do not filter the sample and keep the buret tip below the surface of the sample.
   3.3 Other oxidizable substances, such as organic compounds, ferrous iron and sulfide are positive interferences. Nitrite gives a negative interference by oxidizing sulfite when the sample is acidified; this is corrected by either using a proprietary indicator which eliminates nitrite or by adding sulfamic acid. Copper and possibly other heavy metals catalyze the oxidation of sulfite; EDTA is used to complex metals.
   3.4 A blank must be run.
4. Precision and Accuracy
   4.1 Precision and accuracy data are not available at this time.
5. References
   5.1 The procedure to be used for this determination is found in:

   Standard Methods for the Examination of Water and Wastewater, 13th Edition, p 337-338, Method 158 (1971).

   ASTM Standards, Part 23, Water; Atmospheric Analysis, p 436 Method D-1339 Method C (1973).

TEMPERATURE

STORET NO. 00010

1. Scope and Application

   1.1 This method is applicable to drinking, surface, and saline waters, domestic and industrial wastes.

2. Summary of Method

   2.1 Temperature measurements may be made with any good grade of mercury-filled or dial type centigrade thermometer, or a thermistor.

3. Comments

   3.1 Measurement device should be checked against a precision thermometer certified by the National Bureau of Standards.

4. Precision and Accuracy

   4.1 Precision and accuracy for this method have not been determined.

5. Reference

   5.1 The procedure to be used for this determination is found in:
   Standard Methods for the Examination of Water and Wastewater, 13th Edition, p 348, Method 162 (1971).

THRESHOLD ODOR

(Consistent Series Method)

STORET NO. 60°C: 00086
Room Temp: 00085

1. Scope and Application
   1.1 This method is applicable to the determination of threshold odor of drinking, surface, and saline waters, domestic and industrial wastes.
   1.2 Highly odorous samples are reduced in concentration proportionately before being tested. Thus, the method is applicable to samples ranging from nearly odorless natural waters to industrial wastes with threshold odor numbers in the thousands.
2. Summary of Method(1)
   2.1 The sample of water is diluted with odor-free water until a dilution that is of the least definitely perceptible odor to each tester is found. The resulting ratio by which the sample has been diluted is called the "threshold odor number" (T.O.).
   2.2 People vary widely as to odor sensitivity, and even the same person will not be consistent in the concentrations he can detect from day to day. Therefore, panels of not less than five persons, and preferably 10 or more, are recommended to overcome the variability of using one observer.(2)
      2.2.1 As an absolute minimum, two persons are necessary: One to make the sample dilutions and one to determine the threshold odor.
3. Sample Handling and Preservation
   3.1 Water samples must be collected in glass bottles with glass or Teflon-lined closures.
      3.1.1 Plastic containers are not reliable for odor samples and must not be used.
   3.2 Odor tests should be completed as soon as possible after collection of the sample. If storage is necessary, collect at least 1000 ml of sample in a bottle filled to the top. Refrigerate, making sure no extraneous odors can be drawn into the sample as the water cools.
4. Interferences
   4.1 Most tap waters and some waste waters are chlorinated. It is often desirable to determine the odor of the chlorinated sample as well as of the same sample after removal of chlorine. Dechlorination is achieved using sodium thiosulfate in exact stoichiometric quantity.

4.1.1 It is important to check a blank to which a similar amount of dechlorinating agent has been added to determine if any odor has been imparted. Such odor usually disappears upon standing if excess reagent has not been added.

5. Apparatus

5.1 Odor-free glassware: Glassware must be freshly cleaned shortly before use, with non-odorous soap and acid cleaning solution followed by rinsing with odor-free water (6.1). Glassware used in odor testing should be reserved for that purpose only. Rubber, cork, and plastic stoppers must not be used.

5.2 Constant temperature bath: A water bath or electric hotplate capable of maintaining a temperature control of ±1°C for performing the odor test at 60°C. The temperature bath must not contribute any odor to the odor flasks.

5.3 Odor flasks: Glass stoppered 500 ml (Ṩ 32) Erlenmeyer flasks, or wide-mouthed 500 ml Erlenmeyer flasks equipped with Petri dishes as cover plates.

NOTE: Narrow-mouth vessels are not suitable for running odor tests. Potential positive bias due to color and/or turbidity of water sample under observation can be eliminated by wrapping odor flasks in aluminum foil, painting flasks with non-odorous paint, or by using red actinic Erlenmeyer flasks.

5.4 Sample bottles: Glass bottles with glass or Teflon-lined closures.

5.5 Pipets, measuring: 10.0 and 1.0 ml graduated in tenths.

5.6 Graduated cylinders: 250, 200, 100, 50, and 25 ml.

5.7 Thermometer: 0-110°C (±1°C), chemical or metal stem dial type.

5.8 Odor-free water generator: See Figure 1.

6. Reagents

6.1 Odor-free water: Odor-free dilution water must be prepared as needed by filtration through a bed of activated carbon. Most tap waters are suitable for preparation of odor-free waters, except that it is necessary to check the filtered water for chlorine residual, unusual salt concentrations, or unusually high or low pH. All these may affect some odorous samples.

Where supplies are adequate, distilled water avoids these problems as a source of odor-free water. A convenient odor-free water generator may be made as shown in Figure 1. Pass tap or distilled water through the odor-free water generator at a rate of 0.1 liter/minute. When the generator is first started, it should be flushed to remove carbon fines before the odor-free water is used.

6.1.1 The quality of water obtained from the odor-free water generator should be checked daily at the temperature tests are to be conducted (room temperature and/or 60°C). The life of the carbon will vary with the condition and amount of water filtered. Subtle odors of biological origin are often found if moist carbon filters are permitted to stand idle between test periods. Detection of odor in the water coming through the carbon indicates a change of carbon is needed.

7. Procedure

7.1 *Precautions*: Selection of persons to make odor tests should be carefully made. Extreme sensitivity is not required, but insensitive persons should not be used. A good observer has a sincere interest in the test. Extraneous odor stimuli such as those caused by smoking and eating prior to the test or through the use of scented soaps, perfumes, and shaving lotions must be avoided. The tester should be free from colds or allergies that affect odor-response. Frequent rests in an odor-free atmosphere are recommended. The room in which the tests are to be conducted should be free from distractions, drafts, and other odor. In certain industrial atmospheres, a special odor-free room may be required, ventilated by air filtered through activated carbon and maintained at a constant comfortable temperature and humidity. For precise work a panel of five or more testers should be used. The persons making the odor measurements should not prepare the samples and should not know the dilution concentrations being evaluated. These persons should have been made familiar with the procedure before participating in a panel test. Always start with the most dilute sample to avoid tiring the senses with the concentrated sample. The temperature of the samples during testing should be kept within 1 degree of the specified temperature for the test.

7.2 Threshold measurement: The ratio by which the odor-bearing sample has to be diluted with odor-free water for the odor to be just detectable by the odor test is the "threshold odor number" (T.O.). The total volume of sample and odor-free water used in each test is 200 ml. The proper volume of odor-free water is put into the flask first; the sample is then added to the water. Table 1 gives the dilutions and corresponding threshold numbers.

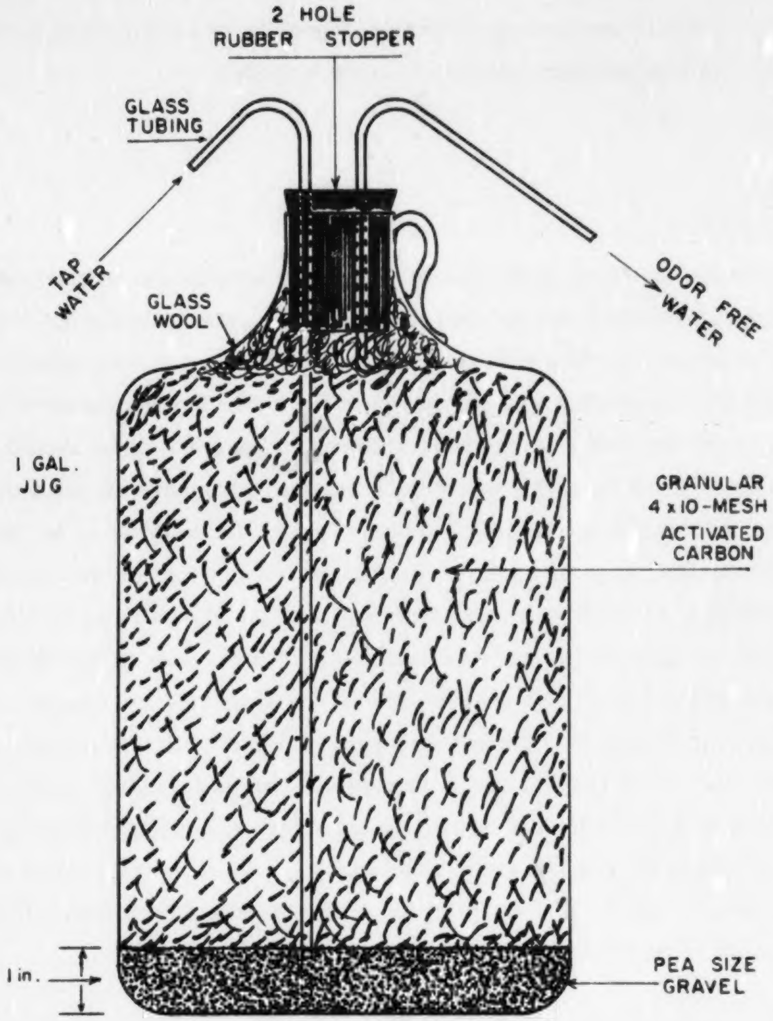
2 HOLE
RUBBER STOPPER
GLASS TUBING
TAP WATER
ODOR FREE WATER
GLASS WOOL
1 GAL. JUG
GRANULAR 4 x 10-MESH ACTIVATED CARBON
1 in.
PEA SIZE GRAVEL

FIGURE 1. ODOR-FREE WATER GENERATOR

Table 1

Threshold Odor Number
Corresponding to Various Dilutions

Sample Volume (ml) Diluted to 200 ml	Threshold Odor Number
200	1
100	2
50	4
25	8
12.5	16
6.3	32
3.1	64
1.6	128
0.8	256

7.3 Determine the approximate range of the threshold odor by:

7.3.1 Adding 200 ml, 50 ml, 12.5 ml, and 3.1 ml of the sample to separate 500 ml glass-stoppered Erlenmeyer flasks containing odor-free water to make a total volume of 200 ml. A separate flask containing only odor-free water serves as the reference for comparison. If run at 60°C, heat the dilutions and the reference in the constant temperature bath at 60°C (±1°C).

7.3.2 Shake the flask containing the odor-free water, remove the stopper, and sniff the vapors. Test the sample containing the least amount of odor-bearing water in the same way. If odor can be detected in this dilution, more dilute samples must be prepared as described in (7.3.3). If odor cannot be detected in the first dilution, repeat the above procedure using the sample containing the next higher concentration of the odor-bearing water, and continue this process until odor is clearly detected.

7.3.3 If the sample being tested requires more extensive dilution than is provided by Table 1, an intermediate dilution is prepared from 20 ml of sample diluted to 200 ml with odor-free water. Use this dilution for the threshold determination. Multiply the T.O. obtained by ten to correct for the intermediate dilution. In rare cases more than one tenfold intermediate dilution step may be required.

7.4 Based on the results obtained in the preliminary test, prepare a set of dilutions using Table 2 as a guide. One or more blanks are inserted in the series, in the vicinity of the expected threshold, but avoiding any repeated pattern. The observer does not know which dilutions are odorous and which are blanks. He smells each flask in sequence, beginning with the least concentrated sample and comparing with a known flask of odor-free water, until odor is detected with utmost certainty.

Table 2

Dilutions for Various Odor Intensities

Sample Volume in Which Odor First Noted			
200 ml	50 ml	12.5 ml	3.1 ml
Volume (ml) of Sample to be Diluted to 200 ml			
200	100	50	(Intermediate Dilution See 7.3.3)
100	50	25	
50	25	12.5	
25	12.5	6.3	
12.5	6.3	3.1	

7.5 Record the observations of each tester by indicating whether odor is noted (+ sign) in each test flask.

For example:

ml sample diluted to 200 ml	12.5	0	25	0	50	100	200
Response	–	–	+	–	+	+	+

8. Calculations

8.1 The threshold odor number is the dilution ratio at which odor is just detectable. In the example above (7.5), the first detectable odor occurred when 25 ml sample was diluted to 200 ml. Thus, the threshold is 200 divided by 25, equals 8. Table 1 lists the threshold numbers that correspond to common dilutions.

8.2 Anomalous responses sometimes occur; a low concentration may be called positive and a higher concentration in the series may be called negative. In such a case, the threshold is designated as that point of detection after which no further anomalies occur.

For instance:

ml sample diluted to 200 ml	6.3	12.5	0	25	50	100
Response	+	–	–	+	+	+
				threshold		

8.3 Calculations of panel results to find the most probable average threshold are best accomplished by appropriate statistical methods. For most purposes, the threshold of a group can be expressed as the geometric mean (G.M.) of the individual thresholds. The geometric mean is calculated in the following manner:

8.3.1 Obtain odor response as outlined in Procedure and record results. For example:

Table 3
Sample Odor Series

ml of Odor-free Water	ml of Sample	Observer Response*				
		1	2	3	4	5
188	12.5	–	–	–	–	–
175	25	–	⊕	–	+	⊕
200	0	–	–	–	–	–
150	50	⊕	+	–	–	+
200	0	–	–	–	–	–
100	100	+	+	⊕	⊕	+
0	200	+	+	+	+	+

*Circled plus equals threshold level.

8.3.2 Obtain individual threshold odor numbers from Table 1.

Observer	T.O.
1	4
2	8
3	2
4	2
5	8

8.3.3 The geometric mean is equal to the nth root of the product of n numbers. Therefore:

$$4 \times 8 \times 2 \times 2 \times 8 = 1024$$

$$\text{and} \quad \sqrt[5]{1024} = \frac{\log 1024}{5} = \frac{3.0103}{5} = 0.6021$$

and anti-log of 0.6021 = 4 = T.O.

9. Precision and Accuracy

9.1 Precision and accuracy data are not available at this time.

9.2 A threshold number is not a precise value. In the case of the single observer, it represents a judgment at the time of testing. Panel results are more meaningful because individual differences have less influence on the result. One or two observers can develop useful data if comparison with larger panels has been made to check their sensitivity. Comparisons of data from time to time or place to place should not be attempted unless all test conditions have been carefully standardized and some basis for comparison of observer intensities exists.

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TURBIDITY

STORET NO. 00076

1. Scope and Application

   1.1 This method is applicable to drinking, surface, and saline waters in the range of turbidity from 0 to 40 nephelometric turbidity units (NTU).

   NOTE 1: NTU's are considered comparable to the previously reported Formazin Turbidity Units (FTU) and Jackson Turbidity Units (JTU).

2. Summary of Method

   2.1 The method is based upon a comparison of the intensity of light scattered by the sample under defined conditions with the intensity of light scattered by a standard reference suspension. The higher the intensity of scattered light, the higher the turbidity. Readings, in NTU's, are made in a nephelometer designed according to specifications outlined in Apparatus 5. A standard suspension of Formazin, prepared under closely defined conditions, is used to calibrate the instrument.

      2.1.1 Formazin polymer is used as the turbidity reference suspension for water because it is more reproducible than other types of standards previously used for turbidity standards.

3. Sample Handling and Preservation

   3.1 Samples taken for turbidity measurements should be analyzed as soon as possible. Preservation of samples is not recommended.

4. Interferences

   4.1 The presence of floating debris and coarse sediments which settle out rapidly will give low readings. Finely divided air bubbles will affect the results in a positive manner.

   4.2 The presence of true color, that is the color of water which is due to dissolved substances which absorb light, will cause turbidities to be low, although this effect is generally not significant with finished waters.

5. Apparatus

   5.1 The turbidimeter shall consist of a nephelometer with light source for illuminating the sample and one or more photo-electric detectors with a readout device to indicate the intensity of light scattered at right angles to the path of the incident light. The turbidimeter should be so designed that little stray light reaches the detector in the absence of turbidity and should be free from significant drift after a short warm-up period.

5.2 The sensitivity of the instrument should permit detection of turbidity differences of 0.02 unit or less in waters having turbidities less than 1 unit. The instrument should measure from 0 to 40 units turbidity. Several ranges will be necessary to obtain both adequate coverage and sufficient sensitivity for low turbidities.

5.3 The sample tubes to be used with the available instrument must be of clear, colorless glass. They should be kept scrupulously clean, both inside and out, and discarded when they become scratched or etched. They must not be handled at all where the light strikes them, but should be provided with sufficient extra length, or with a protective case, so that they may be handled.

5.4 Differences in physical design of turbidimeters will cause differences in measured values for turbidity even though the same suspension is used for calibration. To minimize such differences, the following design criteria should be observed:

5.4.1 Light source: Tungsten lamp operated at not less than 85% of rated voltage or more than rated voltage.

5.4.2 Distance traversed by incident light and scattered light within the sample tube: Total not to exceed 10 cm.

5.4.3 Angle of light acceptance of the detector: Centered at 90° to the incident light path and not to exceed ±30° from 90°.

5.4.4 Maximum turbidity to be measured: 40 units.

5.5 The Hach Turbidimeter, Model 2100 and 2100 A, is in wide use and has been found to be reliable; however, other instruments meeting the above design criteria are acceptable.

6. Reagents

6.1 Turbidity-free water: Pass distilled water through a 0.45μ pore size membrane filter if such filtered water shows a lower turbidity than the distilled water.

6.2 Stock turbidity suspension:

Solution 1: Dissolve 1.00 g hydrazine sulfate, $(NH_2)_2 \cdot H_2SO_4$, in distilled water and dilute to 100 ml in a volumetric flask.

Solution 2: Dissolve 10.00 g hexamethylenetetramine in distilled water and dilute to 100 ml in a volumetric flask.

In a 100 ml volumetric flask, mix 5.0 ml Solution 1 with 5.0 ml Solution 2. Allow to stand 24 hours at 25 ± 3°C, then dilute to the mark and mix.

6.3 Standard turbidity suspension: Dilute 10.00 ml stock turbidity suspension to 100 ml with turbidity-free water. The turbidity of this suspension is defined as 40 units. Dilute portions of the standard turbidity suspension with turbidity-free water as required.

6.3.1 A new stock turbidity suspension should be prepared each month. The standard turbidity suspension and dilute turbidity standards should be prepared weekly by dilution of the stock turbidity suspension.

7. Procedure

7.1 Turbidimeter calibration: The manufacturer's operating instructions should be followed. Measure standards on the turbidimeter covering the range of interest. If the instrument is already calibrated in standard turbidity units, this procedure will check the accuracy of the calibration scales. At least one standard should be run in each instrument range to be used. Some instruments permit adjustments of sensitivity so that scale values will correspond to turbidities. Reliance on a manufacturer's solid scattering standard for setting overall instrument sensitivity for all ranges is not an acceptable practice unless the turbidimeter has been shown to be free of drift on all ranges. If a pre-calibrated scale is not supplied, then calibration curves should be prepared for each range of the instrument.

7.2 Turbidities less than 40 units: Shake the sample to thoroughly disperse the solids. Wait until air bubbles disappear then pour the sample into the turbidimeter tube. Read the turbidity directly from the instrument scale or from the appropriate calibration curve.

7.3 Turbidities exceeding 40 units: Dilute the sample with one or more volumes of turbidity-free water until the turbidity falls below 40 units. The turbidity of the original sample is then computed from the turbidity of the diluted sample and the dilution factor. For example, if 5 volumes of turbidity-free water were added to 1 volume of sample, and the diluted sample showed a turbidity of 30 units, then the turbidity of the original sample was 180 units.

7.3.1 The Hach Turbidimeters, Models 2100 and 2100A, are equipped with 5 separate scales: 0-0.2, 0-1.0, 0-100, and 0-1000 NTU. The upper scales are to be used only as indicators of required dilution volumes to reduce readings to less than 40 NTU.

NOTE 2: Comparative work performed in the MDQAR Laboratory indicates a progressive error on sample turbidities in excess of 40 units.

8. Calculation

8.1 Multiply sample readings by appropriate dilution to obtain final reading.

8.2 Report results as follows:

NTU	Record to Nearest:
0.0–1.0	0.05
1–10	0.1
10–40	1
40–100	5
100–400	10
400–1000	50
>1000	100

9. Precision and Accuracy

9.1 In a single laboratory (MDQARL), using surface water samples at levels of 26, 41, 75 and 180 NTU, the standard deviations were ±0.60, ±0.94, ±1.2 and ±4.7 units, respectively.

9.2 Accuracy data is not available at this time.

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